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METHODS OF ANALYZING COAL AND COKE

BY

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METHODS OF ANALYZING COAL AND COKE.

By FREDERIC M. STANTON and ARNO C. FIELDNER.

INTRODUCTION.

The Bureau of Mines has received many requests for information relative to the methods in use at its laboratories for analyzing coal and coke and determining the heating value of these fuels. The fuel investigations now being conducted by the Bureau of Mines had their inception in the work undertaken at the Government coal-testing plant erected in 1904, at the Louisiana Purchase Exposition, in St. Louis, and the coal-analysis methods used by the Bureau of Mines are essentially those that were originally adopted by the chemists of the coal-testing plant and were followed in the subsequent chemical work of the Government fuel-testing plants at St. Louis, Mo., Norfolk, Va., and Pittsburgh, Pa. This paper describes the original methods (which were those recommended by the committee on coal analysis of the American Chemical Society) and such modifications and changes as experience has shown advisable. Grateful acknowledgment is made of many valuable suggestions and criticisms received from N. W. Lord, late director of the School of Mines at Ohio State University, and from E. E. Somermeier, professor of metallurgy at the same university, to whom the development of the methods now used by the Bureau of Mines is chiefly due.

PRELIMINARY TREATMENT OF SAMPLES.

The coal samples are received at the laboratory in galvanized-iron cans that contain when full about 3 pounds of coal. Each can has a close-fitting screw cap, and is made practically moisture-tight by a piece of electrician's tape wrapped around the joint between the cap and the top of the can. The method of collecting and shipping a sample is described in Technical Paper 1 of the Bureau of Mines.[a] Immediately after a sample is received at the laboratory, it is given a laboratory number, is removed from the can, and is placed in a weighed tin pan about 9½ inches in diameter and 1¼ inches deep. The tin pan containing the sample is placed in a large drying oven

[a] Holmes, J. A., The sampling of coal in the mine. 1911. 18 pp.

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(fig. 1), in which a temperature of 30° to 35° C. is maintained. Through this oven a current of warm air is drawn by means of an ordinary desk fan mounted on top of the oven.

The sample is dried under these conditions until the loss in weight between two successive weighings, made 6 to 12 hours apart, does not exceed 0.2 per cent. The purpose of this drying is to reduce the moisture in the sample to such a condition that rapid change in

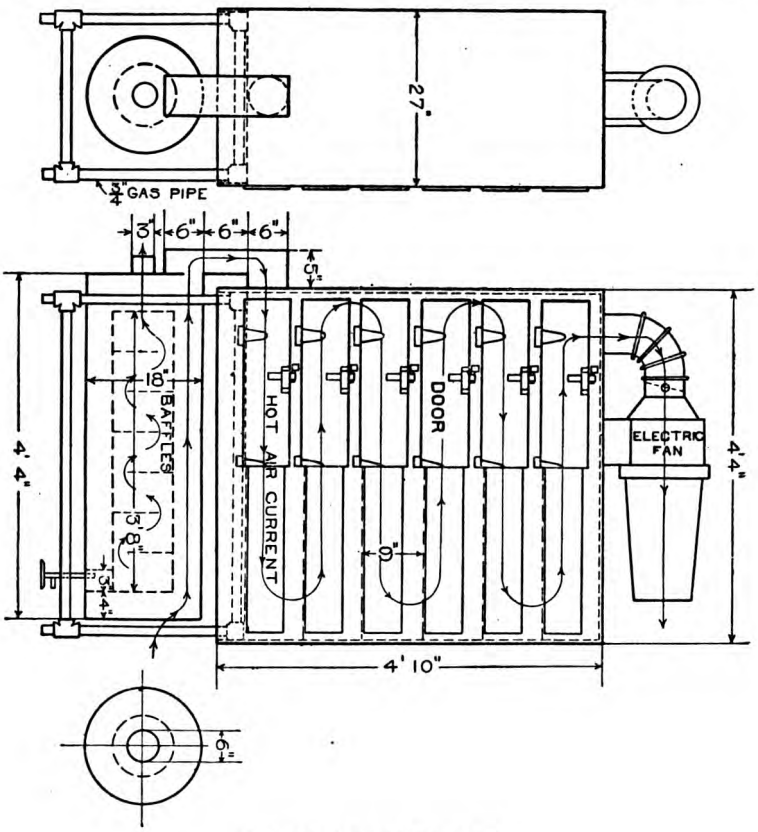

FIGURE 1—Details of drying oven.

weight will not take place while the sample is being handled in the course of analysis.

The loss of weight by air drying is not regarded as an accurate determination, and the "air-drying loss" reported in an analysis simply means that the sample lost the stated percentage of moisture before it came to a condition of moisture equilibrium with the air of the room, at a temperature of 30° to 35° C.

After being air-dried in this oven, the sample is crushed to 10 mesh and finer, and quartered down to about 400 grams. This 400-gram portion is put in the porcelain jar of an Abbe ball-mill, sealed air-tight,

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and ground down to 60 mesh. The jar is about one-third full of well-rounded flint pebbles, 1 inch in diameter, and is rotated about 60 revolutions per minute. The 60-mesh sample is mixed thoroughly, and about 60 grams is taken for analysis. This 60-gram sample is kept in a rubber-stoppered, wide-mouthed bottle, which is numbered and dated.

METHODS OF ANALYSIS.

MOISTURE.

A 1-gram sample of the 60-mesh coal is placed in a weighed $\frac{7}{8}$-inch by $1\frac{3}{4}$-inch porcelain crucible and heated for one hour at 105° C. in

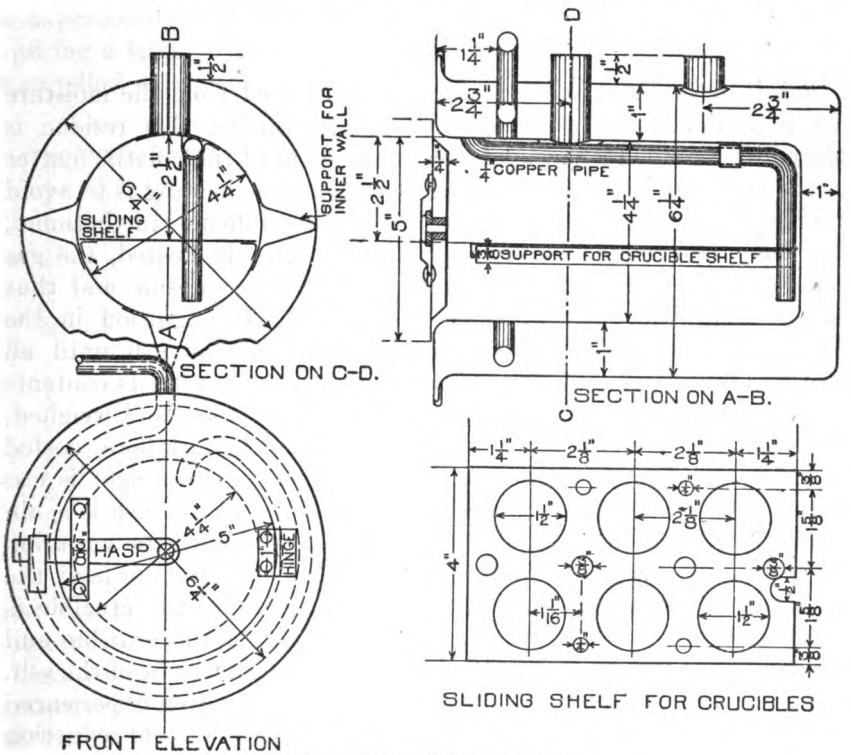

FIGURE 2.—Details of moisture oven.

a constant-temperature oven (fig. 2). The crucible is then removed from the oven, covered, and cooled in a desiccator over sulphuric acid. The loss in weight multiplied by 100 is counted as the percentage of moisture.

The oven used is a double-walled copper cylinder, closed at one end and having a double-walled door at the other. The space between the outer and the inner wall is filled with a solution of glycerin in water (specific gravity, 1.19 at 15° C.), the proportions being so adjusted that the boiling solution maintains a temperature of 105° C.

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in the interior of the oven. There is free circulation space for this glycerin solution on the sides and at one end of the oven. A return condenser keeps the concentration constant. A current of air, dried by passing through sulphuric acid and preheated by passing through a copper tube encircling the oven between the walls, is forced through the inner chamber of the oven over the samples; it takes up moisture from the samples and escapes through a small opening in the door of the oven. The air is forced through the oven at a rate sufficient to change the total volume of air in the oven from 8 to 10 times in one hour. With this oven no trouble is experienced in maintaining a constant temperature of 105° C.

ASH.

Ash is determined in the residue of dried coal from the moisture determination. The porcelain crucible containing this residue is placed in a muffle furnace and slowly heated until the volatile matter in the coal is driven off. The object of this slow heating is to avoid coking the sample and thus making its burning difficult; furthermore, if a coal that is high in volatile matter is rapidly heated, the gas generated has a tendency to explode within the capsule and thus carry off mechanically portions of the ash. The ignition in the muffle is continued, with occasional stirring of the ash, until all particles of carbon have disappeared. The crucible with its contents is then taken from the muffle, cooled in a desiccator, and weighed, after which it is placed in the muffle, heated for half an hour, cooled in a desiccator, and weighed again. If the change in weight is less than 0.0005 gram (if the change is greater than this, the ash is again ignited for 30 minutes and the process is repeated until the variation in weight between two successive ignitions is 0.0005 gram or less), the weight is considered as constant and the weight of the crucible is deducted from the last weighing. The weight of the crucible and ash minus the weight of the crucible is taken as the weight of the ash. In the case of coals high in iron, some difficulty is often experienced in ignition to constant weight, because of the oxidation and reduction of iron oxides.

Ash as determined by this method represents the ignited mineral matter in coal.

VOLATILE MATTER.

A 1-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished, 30-gram platinum crucible with a close-fitting cover. The crucible and contents are heated upon a platinum triangle for seven minutes over a Bunsen flame 20 cm. high. The crucible should be so placed in the triangle that its bottom is 6 to 8 cm. above the top of the burner. To protect the crucible from the

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effects of drafts, it is put in a sheet-iron chimney (fig. 3) of special design. After being heated seven minutes the crucible is cooled and weighed. The loss in weight minus the weight of moisture determined at 105° C. times 100 equals the percentage of volatile matter.

It should be clearly understood that the volatile matter thus determined does not represent any definite compound in the coal. The method of determination is wholly conventional, and any variation in temperature or rate of heating will change the amount of volatile matter determined. Even with strict adherence to the official method, variations as large as 2 per cent are likely to occur in different laboratories where different kinds of gas are used, as is shown by the experiments of Fieldner and Davis.[a] Natural gas, because of its requiring a larger proportion of air for complete combustion, should be supplied at a pressure of not less than 10 inches of water to a

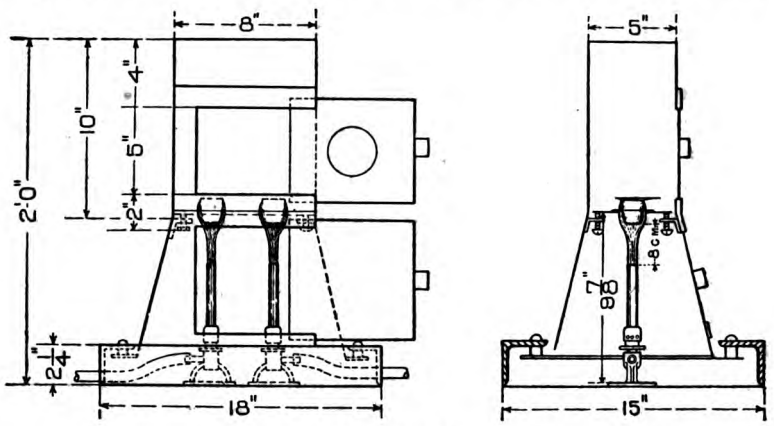

FIGURE 3.—Stand for burner.

good natural-gas burner admitting ample air; otherwise the flame temperature will be too low.

Lignites and coals high in moisture must be heated at a low temperature until all the moisture is driven out in order to avoid mechanical losses from material thrown out of the crucible by the rapid escape of steam and volatile matter.[b] This preliminary heating for four to six minutes is followed by the usual seven-minute application of the full 20-cm. flame.

SULPHUR.

Sulphur is determined by the Eschka method. "Eschka mixture" is made by thoroughly mixing light calcined magnesium oxide (MgO), two parts, with anhydrous sodium carbonate (Na_2CO_3) one part. A 1-gram sample of 60-mesh coal is thoroughly mixed in a 30-c. c.

[a] Jour. Ind. and Eng. Chem., vol. 2, July, 1910, p. 304.
[b] U. S. Geol. Survey Bull. 323, pp. 6-7.

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platinum crucible with about 2 grams of Eschka mixture, and about ½ gram of Eschka mixture is spread over the top to form a cover. The crucible with its contents is placed on a triangle in a slanting position and the mixture is burned out over an alcohol, gasoline, or natural-gas flame. Artificial gas as a rule contains so much sulphur that its use may introduce an error in the determination, owing to the uncertainty regarding the quantity of sulphur taken up by the mixture. In starting the burning a very low flame must be used to avoid driving off volatile matter so fast that the sulphur escapes unburned. Even a small loss of sulphur dioxide (SO_2) may be detected by its pungent odor. The contents of the crucible should never be heated hot enough to cause the blackening of the Eschka-mixture cover.

After the crucible has been heated very slowly and cautiously for about 30 minutes the heat is increased, and after the crucible becomes red hot the contents are stirred occasionally until all black particles are burned out, a condition which indicates that the process is complete. The crucible and contents are then allowed to cool, and the contents are transferred to a 200-c. c. beaker and digested with 75 c. c. of hot water for at least 30 minutes. Filtration into a 300-c. c. beaker follows; the insoluble residue is washed twice with hot water by decantation, and after being transferred to the filter paper is washed with small quantities of hot water until the volume of solution in the 300-c. c. beaker is about 200 c. c. About 4 c. c. of saturated bromine water (or a slight excess) and enough concentrated hydrochloric acid (HCl) to make the solution slightly acid are added. The solution is next boiled, and the sulphur is precipitated as barium sulphate ($BaSO_4$) by adding, slowly from a pipette with constant stirring, 20 c. c. of a hot 5 per cent solution of barium chloride ($BaCl_2$). The solution containing the precipitate is allowed to stand for at least two hours at a temperature just below boiling. It is then filtered through an ashless filter paper and washed first with hot water containing 1 c. c. of hydrochloric acid (HCl) per liter, and then with pure hot water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Test for excess barium chloride is made by adding a few drops of sulphuric acid solution to the filtrate. The precipitate is then ignited in a weighed porcelain crucible, free access of air being allowed and the paper being folded over the precipitate only loosely to prevent spattering. The paper should be smoked off very gradually at first and the final heating should not be above a dull redness. After the paper is burned off completely the heating is continued for a few minutes, when the crucible is cooled and weighed. The weight of barium sulphate multiplied by 13.74 equals the percentage of sulphur in the sample.

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CARBON AND HYDROGEN.

The determination of carbon and of hydrogen is made from a weighed quantity of sample in a 25-burner combustion furnace of the Glaser type. The products of combustion are thoroughly oxidized by being passed over red-hot copper oxide and lead chromate, and are fixed by absorbing the water in a weighed Marchand tube filled with granular calcium chloride ($CaCl_2$) and by absorbing the carbon dioxide in a Liebig bulb containing a 30 per cent solution of potassium hydroxide (KOH).

The apparatus used consist of a purifying train, in duplicate, a combustion tube in the furnace, and an absorption train. The purifying train consists of the following purifying reagents arranged in order of passage of air and oxygen through them: Sulphuric acid, potassium hydroxide solution, soda lime, and granular calcium chloride. One of the trains is for air and one for oxygen. In the sulphuric-acid and potassium-hydroxide scrubbing bottles the air and the oxygen are made to bubble through about 5 mm. of the purifying reagent. Both purifying trains are connected to the combustion tube by a Y tube, the joint being made tight by a rubber stopper.

The combustion tube is made of hard Jena glass. Its internal diameter is about 15 mm., and its total length is 1 meter. The first 30 cm. of the tube is empty; following this empty space is an asbestos plug (acid washed and ignited) or in its place a roll of copper gauze may be used; the next 40 cm. is filled loosely with copper-oxide wire; a second asbestos plug separates the wire from 10 cm. of fused lead chromate, which is held in place by another asbestos plug 20 cm. from the end of the tube. The end of the tube is drawn out for rubber-tubing connection with the absorption train.

The absorption train consists, first, of a Marchand tube filled with granular calcium chloride ($CaCl_2$) to absorb moisture. This tube is followed by a Liebig bulb containing a 30 per cent potassium-hydroxid (KOH) solution, in which any possible impurities, as ferrous iron or nitrates, have been oxidized by a little potassium permanganate ($KMnO_4$). A guard tube, containing soda lime and granular calcium chloride, is attached to the Liebig bulb to absorb any carbon dioxide escaping the potassium-hydroxide solution and any water evaporating from that solution.

The train is connected to an aspirator which draws the products of combustion through the entire train. A guard tube of calcium chloride prevents moisture from running back into the absorption train. The suction is maintained constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber

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connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. The connections are made as tight as possible. The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there are no more than five bubbles per minute in the Mariotte flask the apparatus is considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, a blank is run by aspirating about 1 liter of air through the train, which is heated in the same manner as if a determination on coal were being made. If the Liebig bulb and the tube containing calcium chloride show a change in weight of less than 0.5 mg. the apparatus is in proper condition for use.

A 0.2-gram sample (crushed to 60-mesh) is weighed into a platinum or porcelain boat. The boat and sample are placed in a glass weighing tube closed with a stopper to prevent moisture changes. The absorption tubes are connected and the boat and sample are transferred from the weighing tube to the combustion tube, which should be cool for the first 30 cm. The copper oxide should be red hot and the lead chromate at a dull-red heat. The transfer of the boat from weighing tube to combustion tube should be made as rapidly as possible. As soon as the boat is in place (near the asbestos plug at the beginning of the copper oxide) the stopper connecting with the purifying train is inserted and the aspiration started with pure oxygen gas at the rate of three bubbles per second. One burner is turned on about 10 cm. back from the boat, and the aspiration is continued carefully until practically all the moisture is expelled from the sample. The heat is then increased very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back into the purifying train. The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited; then the temperature can be increased rapidly, but care should be taken not to melt the combustion tube. The aspiration with oxygen is continued for two minutes after the sample ceases to glow, when the heat is then turned off and about 1,200 c. c. of air is aspirated. The absorption bulbs are then disconnected and weighed. The increase in weight of the calcium chloride tube times 55.55 equals the percentage of hydrogen. The increase in weight of the potassium hydroxide bulbs times 136.36 equals the percentage of carbon. The ash in the boat is weighed and carefully inspected for any unburned carbon which would destroy the value of the determination.

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NITROGEN.

The well-known Kjeldahl method is used in determining nitrogen. One gram of the coal sample is boiled with 30 c. c. of concentrated sulphuric acid (H_2SO_4) and 0.6 gram of mercury until all particles of coal are oxidized and the solution nearly colorless. The boiling should be continued at least two hours after the solution has reached the straw-colored stage; then crystals of potassium permanganate ($KMnO_4$) are added, a few at a time, until a permanent green color remains. After cooling, the solution is diluted to about 200 c. c. with cold water. Twenty-five cubic centimeters of potassium sulphide (K_2S) solution (40 grams K_2S per liter) is added to precipitate the mercury; to prevent bumping 1.0 gram of granular zinc, and, to prevent frothing, a piece of paraffin about the size of a brass 1-gram weight are also added. Enough saturated sodium hydroxide (NaOH) solution (usually 80 to 100 c. c.) to make the solution distinctly alkaline is next added and the flask is at once connected with the condenser. The ammonia (NH_3) is distilled over into a measured amount of standard sulphuric acid solution, to which has been added sufficient cochineal indicator for titration. The solution is distilled until about 200 c. c. of distillate has passed over, and the distillate is titrated with standard ammonia (NH_4OH) solution (20 c. c. NH_4OH solution = 10 c. c. H_2SO_4 solution = 0.05 gram nitrogen).

The transfer to a distillation flask may be avoided by the use of a 500 c. c. Kjeldahl flask for digestion of the coal, connection being made direct from the Kjeldahl digestion flask to the condensing apparatus.

PHOSPHORUS.

For the determination of phosphorus in coal or coke, a sample weighing 6.52 grams is burned to ash in the muffle furnace. The ash is mixed with four to six times its weight of sodium carbonate plus 0.2 gram of sodium nitrate, and is fused at the highest temperature of the blast lamp. The fused mass is dissolved in water, acidified, and evaporated to dryness. The residue is taken up in hydrochloric acid, and the phosphorus determined in the usual way, either by weighing or by titrating the yellow precipitate with permanganate.

DETERMINATION OF THE CALORIFIC VALUE OF COAL.

Determination of the calorific value of coal is made with the bomb calorimeter. The method used is applicable to the Mahler, Atwater, Williams, and Emerson bomb calorimeters, all of which are in use in the laboratories of the bureau. The following is a brief description of the details of operation:

A 1-gram sample of coal (60-mesh) is placed in a platinum tray, the bottom of which is covered with a piece of asbestos paper that

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has been washed and ignited. The use of this asbestos mat avoids trouble in completely burning anthracite coal. One of the platinum terminals of the firing circuit is attached to the tray. The terminals are connected by a piece of iron wire (platinum wires should be used when the bomb is platinum-lined) 105 mm. long, 0.16 mm. in diameter, and weighing about 13 mg. The ends of the wire are attached to the platinum terminals, which must be clean, simply by wrapping the wire tightly around them. The iron wire is bent down so as to touch the coal sample on the mat within the tray. The tray is then placed in the bomb and the lid screwed down tightly against the lead gasket. Oxygen is forced into the bomb until the manometer recording the pressure within the bomb reads 18 to 20 atmospheres, when the needle-point valve is closed just tight enough to prevent leakage of gas. The oxygen must be admitted very slowly to avoid blowing any particles of coal dust out of the tray. With some extremely light materials, such as peat, it is best to briquet the sample and take a weighed portion of the broken briquets instead of using the powdered sample.

The bomb filled with oxygen is placed in the brass bucket containing 2,000 to 2,500 grams of distilled water, depending upon the type of calorimeter used, the bucket having been previously placed in the insulated jacket. The stirring apparatus is adjusted so that it touches neither bucket nor bomb, and the thermometer is inserted so that the bulb is about 5 cm. from the bottom of the bucket and is in contact with no metal parts of the apparatus. The outside terminals of the bomb are connected with wires leading to the switch. After the stirrer has been in motion for about a minute, or when the water has been thoroughly mixed, the first reading of the thermometer is taken by means of a reading telescope attached to a cathetometer. The thermometer is graduated to 0.01° C., and the readings can be interpolated to 0.001° C. For the accurate calorimetric work the thermometers should be calibrated to 0.001° C. The stirring should be continued at a uniform rate throughout the determination, and should be sufficiently rapid to insure thorough mixing.

The actual determination may be divided into three periods—the preliminary period, the combustion period, and the final period. The preliminary period usually requires five readings taken one minute apart, or until the rate of change per minute is nearly constant. After taking the fifth reading the current at 75 volts is turned on for about one-half second. This is the beginning of the combustion period. The first two readings in this period are taken one-half minute apart because the change in temperature is so great. The temperature rises to a maximum and then begins to fall; after its rate of fall becomes uniform, readings are taken every minute for five or six minutes. The final reading of the combustion period is the first reading after the rate of fall becomes uniform.

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The following figures are from an actual determination and show the method of calculating the result, and the corrections applied:

Method of calculating from calorimeter readings.

[Sample No. 10743. Weight 1.0000 gram.]

Time. p. m.	Readings. °C.			
1.00				
.54	23.874	.0058	rate of change in preliminary period.	26.463
.55	23.879			23.897
.56	23.885		Observed temperature change.....	2.566
.57	23.892		Thermometer correction.....	.002
.58	23.897	+[a].0058		2.564
		+[b].0027	Radiation loss.....	.0066
				2.5706
.58½	24.160	+[a].0049	Water equivalent.....	3000
		+[b].0014		
.59	25.430	+[a].0008	Total heat developed.....(calories)..	7,711.8
		+[b].0006	Correction.....	41.4
.60	26.280	−[a].0020	Heat developed by combustion of sample .....(calories)..	7,670.4
		−[b].0023		
2.01	26.439	−[a].0025		
		−[b].0026		
.02	26.463	−[a].0026		
		−[b].0026		
.03	26.466	−[a].0026		
		−[b].0026		
		−.0066	algebraic sum.	
.04	26.463			
.05	26.460			
.06	26.458	−.0026	rate of change in final period.	
.07	26.455			
.08	26.454			
.09	26.450			

	Calories.
Wire burned=11.2 mg.	=19.0
Titer (1 c. c.=5 cal.), 2.5 c. c.	=12.5
Sulphur (0.01 gm.=13 cal.), 0.0076 gm.	= 9.9
Room temperature=24°C.	41.4

The reading 23.874°, taken at 1.54 p. m., is the first reading of the preliminary period. The temperature reading 23.897° is the last reading of the preliminary period and was taken at 1.58 p. m., 4 minutes after the first reading; hence 23.897°−23.874°=0.023°, total change in temperature during the preliminary period; also 0.023°÷4=0.0058°, rate of change per minute during the preliminary period.

The rate of change per minute in the final period is found in like manner to be −0.0026°; hence +0.0058°−(−0.0026°)=0.0084°, change in rate during the combustion period.

[a] Computed rate per minute of temperature change at each reading.
[b] Temperature correction for heat loss during each interval.

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The observed change in temperature during the combustion period is 2.564°; the change in rate per degree of temperature change in the combustion period is therefore equal to $\frac{0.0084°}{2.564°} = 0.0033°$.

The change in temperature during the first half minute of the combustion period is 0.273°, and

$0.273° \times 0.0033° = .0009°$, change in rate during first half minute of combustion period.

$0.0058° - 0.0009° = .0049°$, rate of temperature change at reading at $1.58\frac{1}{2}$ p. m.

The rate of change for each succeeding reading in the combustion period is calculated in the same way.

The temperature correction for the heat loss during the half-minute readings is made by dividing the algebraic sum of the rates by 4, and for the minute readings the algebraic sum is divided by 2, because the temperature correction for heat loss during each interval is the mean rate per minute of temperature change multiplied by the time of the interval in minutes. For example, at 1.58 p. m. the rate per minute of temperature change is +0.0058°, and at $1.58\frac{1}{2}$ the rate per minute of temperature change is +0.0049°; therefore the mean rate per minute of temperature change for the one-half minute interval is $\frac{0.0058 + (+0.0049)}{2} = +0.0054°$, and $\frac{1}{2} \times (+0.0054) = +0.0027$, which is the correction for heat loss taking place during the half-minute interval. The algebraic sum of all the temperature corrections for heat loss during each interval is added to the observed temperature change after corrections have been made for the errors in the thermometer; this figure multiplied by the water equivalent of the apparatus gives the total heat developed. Further corrections must be deducted for heat due to formation of aqueous nitric acid and sulphuric acid and to combustion of the iron wire. The correction for iron wire is 1.7 calories per milligram. The correction for sulphur burned to sulphuric acid is 13 calories per 0.01 gram of sulphur. The correction for nitrogen to aqueous nitric acid is made by titrating the acidity of the bomb liquor with standard ammonia solution (0.00574 gram NH_3 per c. c.), and is equivalent to 5 calories per cubic centimeter.

After the combustion of the coal in the calorimeter the bomb is washed out thoroughly and the washings are titrated with standard ammonia solution (0.00574 gram per c. c.), methyl orange being used as an indicator. The acidity is due to the nitric acid (HNO_3) formed from the nitrogen of the coal and the nitrogen of the air in the bomb, and also to the sulphuric acid formed from the combustion of the sulphur in the coal. The sulphur can be easily determined

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by precipitation as barium sulphate. It is convenient to make the ammonia solution of such strength that 1 cubic centimeter is equivalent to 0.00473 gram of nitrogen, for this weight of nitrogen burned to nitrogen pentoxide (N_2O_5) plus water generates 5 calories of heat. The figures are derived as follows:

The calorific value of nitrogen burning to N_2O_5 + water is 1,058 calories per gram.

1,058 calories : 5 calories : : 1 gram : 0.00473 gram.

Therefore 0.00473 gram of nitrogen generates 5 calories of heat when burned to aqueous nitric acid.

The ammonia solution is made up according to the equation

$$HNO_3 + NH_3 = NH_4NO_3.$$

Since N = 14, and NH_3 = 17,

$$14 : 17 = 0.00473 \text{ gram} : 0.00574 \text{ gram}.$$

Therefore 0.00574 gram of NH_3 is equivalent to 0.00473 gram of nitrogen, which when burned to aqueous HNO_3 generates 5 calories of heat. The standard solution contains 5.74 grams of NH_3 per liter. The solution, when used to titrate the bomb liquor after combustion of a coal sample, must satisfy not only the nitric acid formed, but also any sulphuric acid resulting from the combustion of the sulphur in the coal.

The strength of the ammonia solution in terms of sulphur in the form of sulphuric acid (H_2SO_4) is determined by the following equation:

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

$$2NH_3 : S = 34 : 32 = 0.00574 \text{ gram } NH_3 : 0.0054 \text{ gram S}.$$

The heat of combustion of sulphur to aqueous H_2SO_4 is 4,450 calories per gram of sulphur. This reaction takes place in the bomb calorimeter, when the fuel is burned in an atmosphere of oxygen under high pressure.

In the ordinary combustion of coal under a boiler, the sulphur burns to sulphur dioxide (SO_2), the heat of formation of which is 2,250 calories per gram of sulphur. The difference between these two calorific values (4,450 calories − 2,250 calories) is 2,200 calories per gram of sulphur. Therefore it is necessary to make a correction of 2,200 calories per gram of sulphur in the calorimeter determinations, owing to the formation of aqueous sulphuric acid. Since 1 c. c. of the ammonia solution is equivalent to 0.0054 gram of sulphur, 0.0054 times 2,200 equals 11.9 calories, the heat correction to be made if all the acidity of the liquor from the bomb represented H_2SO_4.

Hence the ammonia solution containing 0.00574 gram NH_3 per c. c. is equivalent to 5 calories for nitrogen converted to aqueous

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HNO_3 or to 11.9 calories for sulphur converted to aqueous H_2SO_4. A further correction, therefore, must be applied for the sulphur that is determined separately. This correction is a function of the difference between the value of the ammonia solution in terms of sulphur (11.9 calories), and its value in terms of nitrogen (5 calories) or 6.9 calories. The difference, 6.9, divided by 0.0054, the value of 1 c. c. of ammonia solution in grams of sulphur, equals 1,276 calories per gram of sulphur, or 13 calories for each 0.01 gram of sulphur.

The total acidity correction is, then, the cubic centimeters of NH_3 solution multiplied by 5 (the factor for nitric acid) plus the centigrams of sulphur multiplied by 13.

STANDARDIZATION OF THE CALORIMETER.

The first factor to be considered in calorimetric work is the correct determination of the water-equivalent value of the apparatus. This equivalent may be determined by a number of methods, as follows:

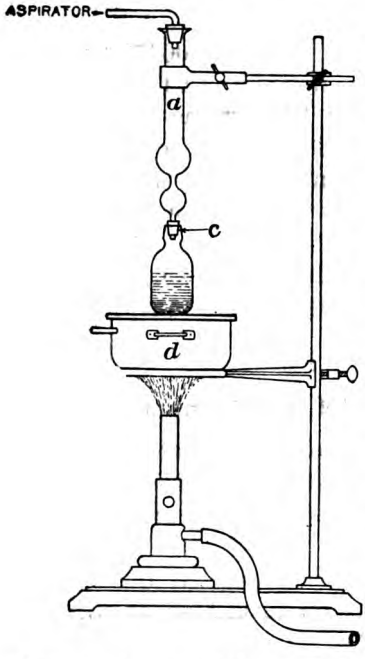

FIGURE 4.—Arrangement of pycnometer.

1. By adding the products of the weight of the different parts of the apparatus times their specific heat.

2. By generating heat within the bomb by passing a measured electric current through a known resistance for a given length of time.

3. By adding definite weights of water at different temperatures to the system and noting the corresponding temperature changes.

4. By varying the quantity of water surrounding the bomb, thus keeping the heat generated within the bomb constant.

5. By the combustion of a substance of known calorific value. This is a very convenient and accurate method of standardization. Samples of pure cane sugar, benzoic acid, and naphthalene may be obtained from the Bureau of Standards.

DETERMINATION OF THE TRUE SPECIFIC GRAVITY OF COAL AND COKE SUBSTANCE.

To determine the true specific gravity of coal and coke substance, the procedure is as follows: A sample of the 60-mesh coal, weighing

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approximately 3.5 grams, is dried at 105° C., and introduced into a 50-c. c. pycnometer with about 30 c. c. of distilled water. In order to avoid loss of particles of the sample during boiling, a one-bulb 6-inch drying tube (*a*, fig. 4) is connected with the pycnometer by means of a small piece of pure gum tubing (*c*). The other end of the drying tube is connected with the aspirator. Suction is applied and the contents of the flask are gently boiled on the water bath (*d*) under partial vacuum for three hours in order to expel all air from the sample. The pycnometer is then detached, almost filled with boiled and cooled water, allowed to cool to the temperature of the balance room, stoppered, and weighed. The temperature of the contents of the pycnometer are taken immediately after weighing. Each pycnometer is accurately calibrated and a table is constructed giving its capacity in grams of water at different temperatures.

The true specific gravity is determined by use of the following formula:

$$\text{True specific gravity} = \frac{W}{W-(W'-P)}$$

in which

W = weight of coke
W′ = weight of pycnometer + coke + water to fill
P = weight of pycnometer + water to fill.

DETERMINATION OF THE APPARENT SPECIFIC GRAVITY.

The apparatus used for determination of the apparent specific gravity consists of a galvanized iron cylinder (fig. 5), which is filled with water to the water line, as indicated in the figure. In the cylinder is immersed a hydrometer made of brass. On the top of the hydrometer are two pans. The upper one is used for weights and the lower for the sample. Below the air buoy is a brass cage perforated with many holes to allow the air to escape when the instrument is immersed. The cage carries the sample when it is weighed under water.

The method of determining the apparent specific gravity is as follows: Brass weights are placed on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. The total weight required is recorded. The weights are removed, and about 500 grams of the sample in lump form (about 1½ to 2 inch cubes) is placed in the copper dish. Brass weights are then added until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air. The sample is then carefully transferred to the brass cage below the buoy. The weights on the upper pan are now adjusted until the instrument again sinks to the mark on the stem. The

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weight required to sink the hydrometer to the mark with no sample on the upper pan nor in the brass cage minus the weight required to

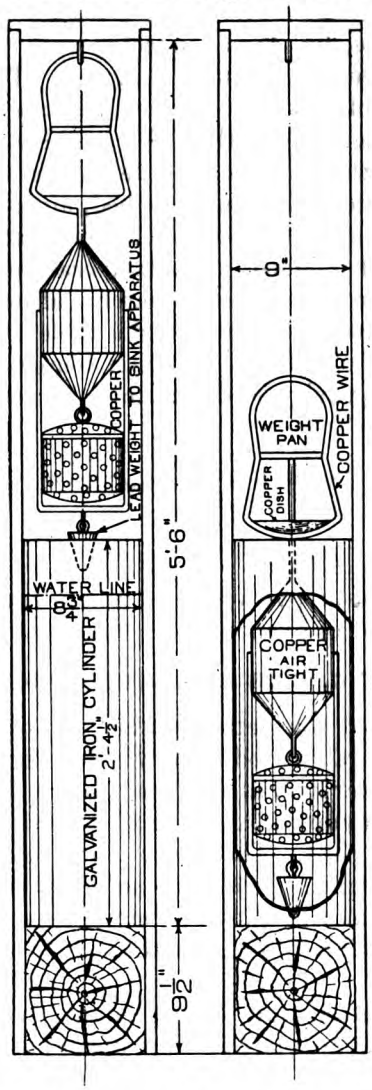

FIGURE 5.—Apparatus for determining apparent specific gravity.

sink it to the mark with the sample immersed in the cage equals the weight of the coke in water. Then,

If the weight of the sample in air $= x$
and the weight of the sample in water $= y$,

the apparent specific gravity $= \frac{x}{x-y}$

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And

$$100 \times \frac{\text{apparent specific gravity}}{\text{true specific gravity}} = \text{percentage by volume of coke substance.}$$

Also,

100 − percentage by volume of coke substance = percentage by volume of cell space.

In making apparent specific gravity determinations of coke the sample should preferably be in lumps of nearly the same size and shape. When the sample is immersed, the hydrometer should be moved rapidly up and down in the water a number of times in order to remove air bubbles. Since coke samples are porous, they take up water rapidly and should not be allowed to remain in contact with water more than five minutes during a determination. By observing the above-mentioned precautions satisfactory results can be obtained. All samples should be thoroughly dry before specific gravity determinations are made.

PUBLICATIONS ON FUEL TESTING.

PUBLICATIONS OF THE BUREAU OF MINES.

The following publications may be obtained without cost by applying to the Director, Bureau of Mines, Washington, D. C.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp. 4 pls.

BULLETIN 5. Washing and coking tests of coal at Denver, Colo., by A. W. Belden, G. R. Delamater, J. W. Groves, and K. M. Way. 1910. 62 pp.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker. 1911. 77 pp., 4 pls.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 51 pp., 1 pl.

BULLETIN 8. The flow of heat through furnace walls, by W. T. Ray and Henry Kreisinger. 1911. 32 pp.

BULLETIN 9. Recent development of the producer-gas power plant in the United States, by R. H. Fernald. 82 pp., 2 pls. Reprint of United States Geological Survey Bulletin 416.

BULLETIN 11. The purchase of coal by the Government under specifications, by George S. Pope. 80 pp. Reprint of United States Geological Survey Bulletin 428.

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BULLETIN 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp.

BULLETIN 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls.

BULLETIN 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908–9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls.

BULLETIN 16. The uses and value of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl.

BULLETIN 19. Physical and chemical properties of the petroleums of the San Joaquin Valley, Cal., by I. C. Allen and W. A. Jacobs; with a chapter on analyses of natural gas from the southern California oil fields, by G. A. Burrell. 1911. 60 pp.

BULLETIN 21. The significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 62 pp. Reprint of United States Geological Survey Bulletin 367.

BULLETIN 24. Binders for coal briquets, by J. E. Mills. 56 pp. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 45 pp., 3 pls. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 28. Experimental work conducted in the laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 49 pp. Reprint of United States Geological Survey Bulletin 323.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

BULLETIN 30. Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907–8, by C. L. Wright. 41 pp., 9 pls. Reprint of United States Geological Survey Bulletin 385.

BULLETIN 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp. Reprint of United States Geological Survey Bulletin 393.

BULLETIN 32. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

BULLETIN 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 49 pp. Reprint of United States Geological Survey Bulletin 403.

BULLETIN 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 32 pp. Reprint of United States Geological Survey Bulletin 412.

BULLETIN 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 28 pp. Reprint of United States Geological Survey Bulletin 402.

BULLETIN 37. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests and some foreign specifications for briquetted fuel, by W. M. F. Gross. 57 pp., 4 pls. Reprint of United States Geological Survey Bulletin 363.

TECHNICAL PAPER 1. The sampling of coal in the mine, by J. A. Holmes. 1911. 18 pp.

TECHNICAL PAPER 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp.

TECHNICAL PAPER 3. Specifications for the purchase of fuel oil by the Government, with directions for sampling oil and natural gas, by I. C. Allen. 1911. 13 pp.

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PUBLICATIONS OBTAINABLE FROM THE SUPERINTENDENT OF DOCUMENTS.

The following technologic publications of the United States Geological Survey can be obtained by sending the price, in cash, to the Superintendent of Documents, Government Printing Office, Washington, D. C.

PROFESSIONAL PAPER 48. Report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1906. In three parts. 1492 pp., 13 pls. $1.50.

BULLETIN 261. Preliminary report on the operations of the coal-testing plant of the United States Geological Survey at the Louisiana Purchase Exposition, in St. Louis, Mo., 1904; E. W. Parker, J. A. Holmes, M. R. Campbell, committee in charge. 1905. 172 pp. 10 cents.

BULLETIN 290. Preliminary report on the operations of the fuel-testing plant of the United States Geological Survey at St. Louis, Mo., 1905, by J. A. Holmes. 1906. 240 pp. 20 cents.

BULLETIN 325. A study of four hundred steaming tests made at the fuel-testing plant, St. Louis, Mo., 1904, 1905, and 1906, by L. P. Breckenridge. 1907. 196 pp. 20 cents.

BULLETIN 332. Report of the United States fuel-testing plant at St. Louis, Mo., January 1, 1906, to June 30, 1907; J. A. Holmes, in charge. 1908. 299 pp. 25 cents.

BULLETIN 336. Washing and coking tests of coal and cupola tests of coke, by Richard Moldenke, A. W. Belden, and G. R. Delamater. 1908. 76 pp. 10 cents.

BULLETIN 362. Mine sampling and chemical analyses of coals tested at the United States fuel-testing plant, Norfolk, Va., in 1907, by J. S. Burrows. 1908. 23 pp. 5 cents.

BULLETIN 368. Washing and coking tests of coal at Denver, Colo., by A. W. Belden, G. R. Delamater, and J. W. Groves. 1909. 54 pp., 2 pls. 10 cents.

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Technical Paper 8a. (Revised ed.)

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PRINCETON, N. J.

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
JOSEPH A. HOLMES, DIRECTOR

METHODS OF ANALYZING COAL AND COKE

BY

FREDERIC M. STANTON

AND

ARNO C. FIELDNER

WASHINGTON
GOVERNMENT PRINTING OFFICE
1913

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NOTE.

Since the publication of the first edition of this paper in January, 1912, the Bureau of Mines has received many inquiries for additional information in regard to details of sampling or analytical work that were not discussed at length in that edition. Moreover, the Bureau of Mines has modified and improved various details of its laboratory practice so that statements made in the first edition of this paper do not apply exactly to all the methods now used. For these reasons it has been decided, in publishing a new edition of the paper, to make radical changes in the text and to add new illustrations. The bureau hopes that in its present form the paper will meet the needs of all persons interested in the analysis of coal and coke.

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METHODS OF ANALYZING COAL AND COKE.

By FREDERIC M. STANTON and ARNO C. FIELDNER.

INTRODUCTION.

The Bureau of Mines has received many requests for information relative to the methods in use at its laboratories for analyzing coal and coke and determining the heating value of these fuels. The fuel investigations now being conducted by the Bureau of Mines had their inception in the work undertaken at the Government coal-testing plant erected in 1904, at the Louisiana Purchase Exposition, in St. Louis, and the coal-analysis methods used by the Bureau of Mines are essentially those that were originally adopted by the chemists of the coal-testing plant and were followed in the subsequent chemical work of the Government fuel-testing plants at St. Louis, Mo., Norfolk, Va., and Pittsburgh, Pa. This paper describes the original methods (which were those recommended by the committee on coal analysis of the American Chemical Society) and such modifications and changes as experience has shown advisable. Grateful acknowledgment is made of many valuable suggestions and criticisms received from N. W. Lord, late director of the School of Mines at Ohio State University, and from E. E. Somermeier, professor of metallurgy at the same university, to whom the development of the methods now used by the Bureau of Mines is chiefly due.

PRELIMINARY TREATMENT OF SAMPLES.

PREPARATION OF LABORATORY SAMPLE WITH PRELIMINARY DRYING.

The coal samples are received at the laboratory in galvanized-iron cans that contain when full about 3 pounds of coal. Each can has a close-fitting screw cap, and is made practically moisture-tight by a piece of electrician's tape wrapped around the joint between the cap and the top of the can. The methods of collecting and shipping samples are described in Technical Paper 1[a] and Bulletin 63[b] of the Bureau of Mines. Immediately after a sample is received at the

[a] Holmes, J. A., The sampling of coal in the mine. 1911. 18 pp.

[b] Pope, G. S., Sampling coal deliveries, and types of Government specifications for the purchase of coal. 1913. 68 pp.

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laboratory, it is given a laboratory number, is removed from the can, and is placed in a weighed tin pan about 9½ inches in diameter and 1¼ inches deep. The tin pan containing the sample is placed in a large drying oven (fig. 1), in which a temperature of 30° to 35° C. is maintained. Through this oven a current of warm air is drawn by means of an ordinary desk fan mounted on top of the oven.

The sample is dried under these conditions until the loss in weight between two successive weighings, made 6 to 12 hours apart, does

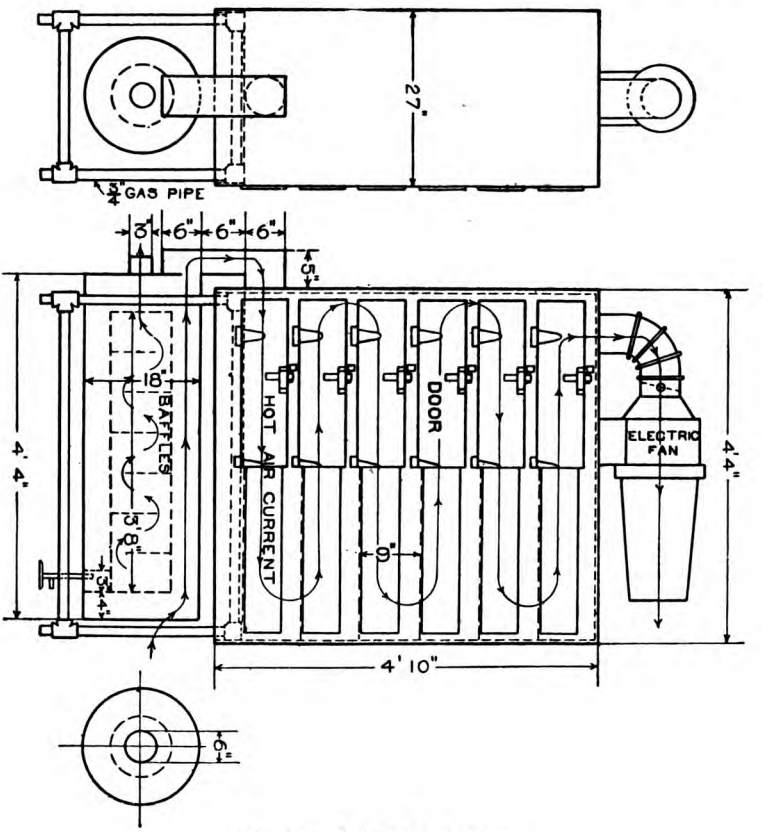

FIGURE 1.—Details of drying oven.

not exceed 0.5 per cent. The purpose of this drying is to reduce the moisture in the sample to such a condition that rapid change in weight will not take place while the sample is being handled in the course of analysis.

The loss of weight by air-drying is not regarded as an accurate determination, and the "air-drying loss" reported in an analysis simply means that the sample lost the stated percentage of moisture before it came to a condition of moisture equilibrium with the air of the room, at a temperature of 30° to 35° C.

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After being air-dried in this oven, the sample is rapidly crushed with a jaw crusher and rolls to 10 mesh and finer, and by quartering is reduced to a portion weighing about 400 grams. This 400-gram portion is put in the porcelain jar of an Abbe ball-mill, sealed air-tight, and ground down to 60 mesh. The jar is about one-third full of well-rounded flint pebbles, 1 inch in diameter, and is rotated about 60 revolutions per minute. The wear of the pebbles and interior of the mill does not increase the ash content appreciably.

Twenty to thirty minutes' rotation suffices for bituminous coal, but some anthracites may require rotation for two hours. When pulverization is complete, the contents of the jar are poured on a half-inch screen and the sample is separated from the pebbles by shaking the screen. The sample is then reduced to about 50 grams by passing it three times through a small riffle sampler. This 50-gram portion is quickly passed through a 60-mesh sieve, and is put in a rubber-stoppered, wide-mouthed, 4-ounce bottle, which is numbered and dated. Usually some coarse particles, amounting to 0.2 to 0.4 per cent of the sample, remain on the sieve. As these particles are apt to consist largely of ash-forming substances, they are reduced to 60 mesh on a bucking board and added to what passed through the sieve.

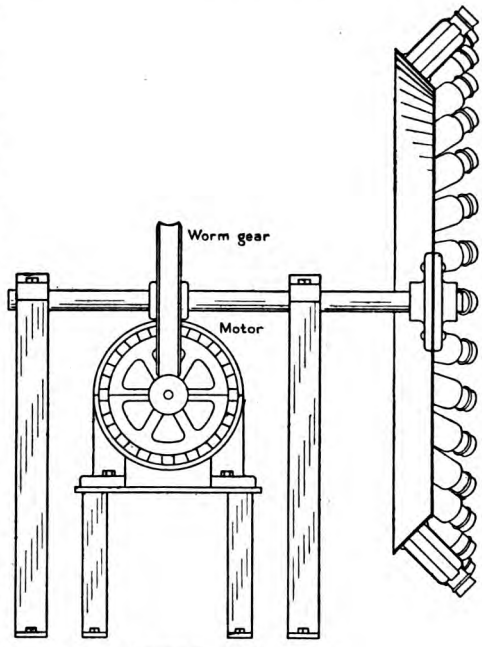

FIGURE 2.—Mixing wheel.

Before portions for the various analytical determinations are weighed the sample is thoroughly mixed. The bottle containing the sample is placed in the mixing wheel,[a] shown in figure 2, and rotated for 20 minutes. The wheel is 30 inches in diameter and revolves 25 times in a minute. The sample bottles are held by spring clips on the periphery of the wheel at an angle of 45° with the axis. The bottles should not be more than half filled, and the speed of rotation should be slow enough to prevent centrifugal action from hindering the thorough mixing of the powdered coal.

[a] Designed by J. D. Davis, chemist, of the Bureau of Mines.

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METHOD OF CALCULATING AND REPORTING ANALYSES.

As all the analytical determinations are made on the air-dried sample, the analysis of the coal as received at the laboratory is calculated from the analysis of the air-dried coal in the following manner:

Calculation from analysis of "air-dried" coal to coal "as received."

$$\text{Moisture}^a \times \frac{(100 - \text{air-drying loss}^a)}{100} + \text{air-drying loss}^a = \text{moisture}^a \text{ "as received."}$$

$$\text{Volatile matter} \times \frac{(100 - \text{air-drying loss})}{100} = \text{volatile matter "as received."}$$

$$\text{Fixed carbon} \times \frac{(100 - \text{air-drying loss})}{100} = \text{fixed carbon "as received."}$$

$$\text{Ash} \times \frac{(100 - \text{air-drying loss})}{100} = \text{ash "as received."}$$

$$\text{Sulphur} \times \frac{(100 - \text{air-drying loss})}{100} = \text{sulphur "as received."}$$

$$\text{Hydrogen} \times \frac{(100 - \text{air-drying loss})}{100} + \tfrac{1}{9} \text{ air-drying loss} = \text{hydrogen "as received."}$$

$$\text{Carbon} \times \frac{(100 - \text{air-drying loss})}{100} = \text{carbon "as received."}$$

$$\text{Nitrogen} \times \frac{(100 - \text{air-drying loss})}{100} = \text{nitrogen "as received."}$$

$$\text{Oxygen} \times \frac{(100 - \text{air-drying loss})}{100} + \tfrac{8}{9} \text{ air-drying loss} = \text{oxygen "as received."}$$

$$\text{Calories} \times \frac{(100 - \text{air-drying loss})}{100} = \text{calories "as received."}$$

A statement of analysis is referred to a moisture-free basis by calculation from the "air-dry" or "as received" analysis in the following manner:

Calculation from "air-dry" or "as received" analysis to "dry coal."

$$\text{Volatile matter} \times \frac{100}{100 - \text{moisture}} = \text{volatile matter in "dry coal."}$$

$$\text{Fixed carbon} \times \frac{100}{100 - \text{moisture}} = \text{fixed carbon in "dry coal."}$$

$$\text{Ash} \times \frac{100}{100 - \text{moisture}} = \text{ash in "dry coal."}$$

$$\text{Sulphur} \times \frac{100}{100 - \text{moisture}} = \text{sulphur in "dry coal."}$$

$$(\text{Hydrogen} - \tfrac{1}{9} \text{ moisture}) \times \frac{100}{100 - \text{moisture}} = \text{hydrogen in "dry coal."}$$

$$\text{Carbon} \times \frac{100}{100 - \text{moisture}} = \text{carbon in "dry coal."}$$

$$\text{Nitrogen} \times \frac{100}{100 - \text{moisture}} = \text{nitrogen in "dry coal."}$$

$$(\text{Oxygen} - \tfrac{8}{9} \text{ moisture}) \times \frac{100}{100 - \text{moisture}} = \text{oxygen in "dry coal."}$$

$$\text{Calories} \times \frac{100}{100 - \text{moisture}} = \text{calories in "dry coal."}$$

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[a] All figures expressed in per cent.

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For making comparisons, coal analyses are sometimes referred to a "moisture and ash free" basis, by calculation from the "air-dry," "as received," or "moisture-free" analyses, in the following manner:

Calculation from "air-dry," "as received," or "moisture-free" analysis to "moisture and ash free" basis.

$$\text{Volatile matter} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{volatile matter referred to "moisture and ash free" basis.}$$

$$\text{Fixed carbon} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{fixed carbon referred to "moisture and ash free" basis.}$$

$$\text{Sulphur} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{sulphur referred to "moisture and ash free" basis.}$$

$$(\text{Hydrogen} - \tfrac{1}{9}\ \text{moisture}) \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{hydrogen referred to "moisture and ash free" basis.}$$

$$\text{Carbon} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{carbon referred to "moisture and ash free" basis.}$$

$$\text{Nitrogen} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{nitrogen referred to "moisture and ash free" basis.}$$

$$(\text{Oxygen} - \tfrac{8}{9}\ \text{moisture}) \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{oxygen referred to "moisture and ash free" basis.}$$

$$\text{Calories} \times \frac{100}{100-(\text{moisture}+\text{ash})} = \text{calories referred to "moisture and ash free" basis.}$$

Calorific values in calories are converted to calorific values in British thermal units (B. t. u.) by multiplying by 1.8.

PREPARATION OF LABORATORY SAMPLE WITHOUT PRELIMINARY AIR-DRYING

The samples (weighing about three pounds) are received in galvanized-iron cans. If the coal is coarser than ¼ inch it is first passed through a chipmunk jaw crusher which reduces to ¼ inch and finer, and then through a roll crusher which reduces it to 20-mesh fineness. Immediately after the material has passed through the rolls a 60 to 100 gram portion is taken for the determination of total moisture and is transferred to a rubber-stoppered, 4-ounce bottle. The remainder of the sample is thoroughly mixed, and is then repeatedly passed through a riffle sampler until reduced to approximately 150 grams. This 150-gram portion is ground to pass a 60-mesh sieve, by means of a planetary-disk pulverizer, again mixed, and reduced with a riffle sampler to about 60 grams. This final sample is preserved in a rubber-stoppered, 4-ounce bottle, which is numbered and dated.

Moisture is determined at 105° C. with 1-gram portions of the 60-mesh sample and with 5-gram portions of the 20-mesh sample, as described on page 12. The analysis of the 60-mesh coal, which has

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become partly air-dried during sampling, is calculated to the dry basis by dividing each result by 1 minus its content of moisture. The analysis of the coal "as received" is computed from the "dry coal" analysis by multiplying by 1 minus the total moisture found in the 20-mesh sample.

RELATIVE MERITS OF THE TWO METHODS OF SAMPLING.

The first method is preferable for the preparation of laboratory samples that are intended for highly accurate analyses. The unavoidable loss of moisture during sampling is less than by the second method, especially in the case of samples of wet or freshly mined coal. Such samples lose moisture rapidly on exposure to air. Air-drying should not be unnecessarily prolonged, otherwise an appreciable loss of heating value from oxidation takes place.

The second method, which is used in the fuel-inspection laboratory of the Bureau of Mines,[a] admits of handling a large number of samples in a short time. The moisture obtained by this method is usually somewhat less than that obtained by the first method. In the case of coals that have lost part of their moisture content through being exposed to the atmosphere, like the usual commercial shipments, this difference need not exceed 0.5 per cent. Wet samples must be partly air-dried. The disk pulverizer is not adapted to the fine grinding of coke and anthracite; the abrasive action of the coke on the iron surface of the disk pulverizer seriously contaminates the sample; and anthracite is heated by the rubbing surfaces to a degree that may change the composition of the sample.

METHODS OF ANALYSIS.

MOISTURE.

A 1-gram sample of the 60-mesh coal is placed in a weighed $\frac{7}{8}$-inch by $1\frac{3}{4}$-inch porcelain capsule (*a*, fig. 3) and heated for one hour at 105° C. in a constant-temperature oven (figs. 3 and 4). The capsule is then removed from the oven, covered with a special flat aluminum cover (*b*, fig. 3), and cooled in a desiccator over sulphuric acid. The loss in weight multiplied by 100 is recorded as the percentage of moisture.

The oven used is a double-walled copper cylinder, closed at one end and having a double-walled door at the other. (Fig. 3.) The space between the outer and the inner wall is filled with a solution of glycerin in water (specific gravity, 1.19 at 15° C.), the proportions being so adjusted that the boiling solution maintains a temperature of 105° C. in the interior of the oven. There is free circulation space for this

[a] See The fuel-inspection laboratory of the Bureau of Mines, by J. D. Davis, in Bull. 41, Bureau of Mines, p. 77.

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glycerin solution on the sides and at one end of the oven. A return condenser (*c*, fig. 3) keeps the concentration constant. A current of air, dried by passing through sulphuric acid (*d*, fig. 3) and preheated by passing through a copper tube encircling the oven between the walls, is forced through the inner chamber of the oven and over the samples; it takes up moisture from the samples and escapes through a small opening in the door of the oven. The air is forced through

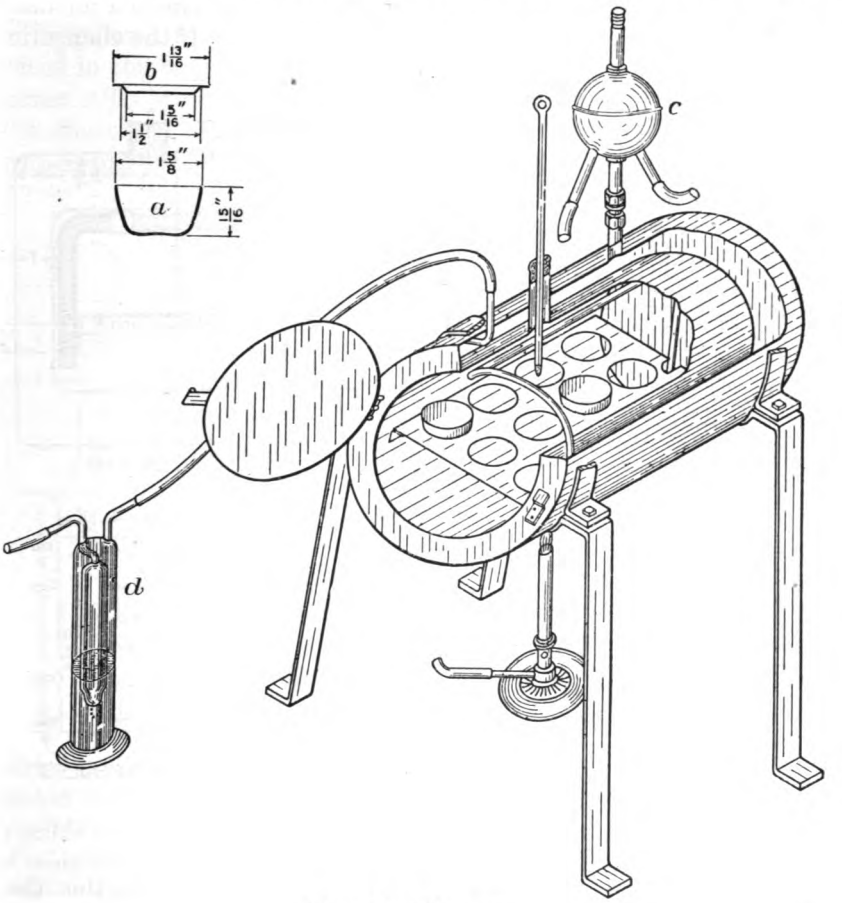

FIGURE 3.—Moisture oven.

the oven at a rate sufficient to change the total volume of air in the oven from 2 to 4 times in one minute. With this oven no trouble is experienced in maintaining a constant temperature of 105° C.

ASH.

Ash is determined in the residue of dried coal from the moisture determination. The porcelain capsule containing this residue is placed in a muffle furnace and slowly heated until the volatile matter in the coal is driven off. The object of this slow heating is to avoid

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coking the sample and thus making its burning difficult; furthermore, if a coal that is high in volatile matter is rapidly heated, the gas generated has a tendency to explode within the capsule and thus carry off mechanically portions of the ash. The ignition in the muffle is continued at a temperature of about 750° C., with occasional stirring of the ash, until all particles of carbon have disappeared. The capsule with its contents is then taken from the muffle, cooled in a desiccator, and weighed, after which it is replaced in the muffle, heated for half an hour, cooled in a desiccator, and weighed again. If the change in

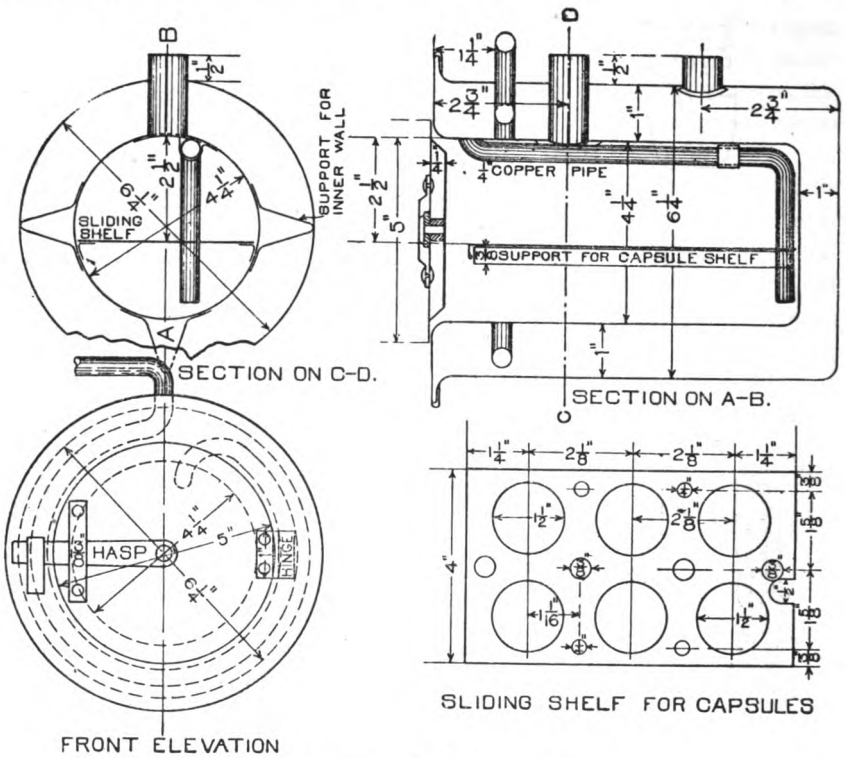

FIGURE 4.—Details of moisture oven.

weight is less than 0.0005 gram (if the change is greater than this, the ash is again ignited for 30 minutes and the process is repeated until the variation in weight between two successive ignitions is 0.0005 gram or less), the weight is considered as constant and the weight of the capsule is deducted from the last weighing. The weight of the capsule and ash minus the weight of the capsule is taken as the weight of the ash. In the case of coals high in iron, some difficulty is often experienced in ignition to constant weight, because of the oxidation and reduction of iron oxides.

Ash as determined by this method represents the mineral matter that remains in coal after ignition.

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VOLATILE MATTER.

A 1-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished, 10-gram (10 c. c.) platinum crucible (*a*, fig. 5) with a close-fitting capsule cover (*b*, fig. 5). The crucible and contents are heated to a temperature of 950° C. upon a platinum or nichrome triangle for seven minutes in the full flame of a No. 3 Meker burner. The gas orifice of the burner is adjusted to give a free-burning flame from 16 to 18 cm. high. The crucible should be so placed in the triangle that its bottom is 2 cm. above the top of the burner. To protect the crucible from the effects of drafts, it is put in a sheet-iron chimney (fig. 5) of special design. The maximum temperature, as measured by a thermocouple whose hot junction is

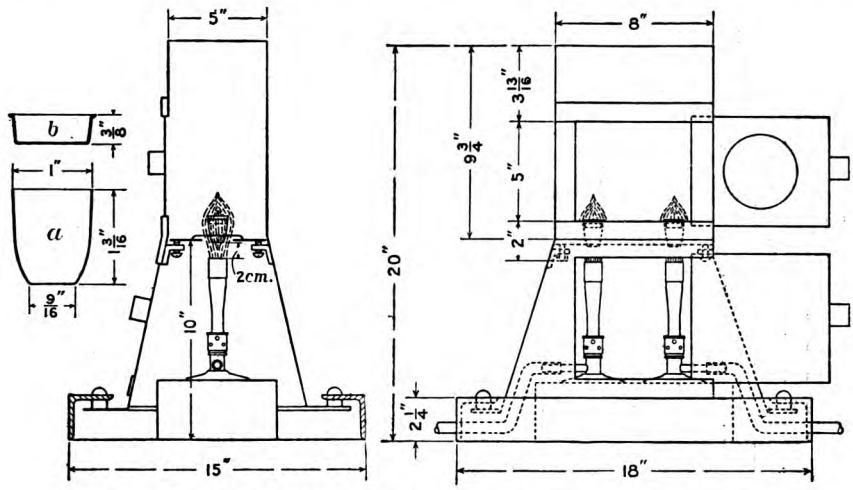

FIGURE 5.—Apparatus for determining volatile matter.

buried in the coal and in contact with the inside surface of the bottom, should be 950° C. After being heated exactly seven minutes, the crucible is cooled and weighed. The loss in weight minus the weight of moisture determined at 105° C. times 100 equals the percentage of volatile matter.

Lignites and coals high in moisture must be heated at a low temperature until all the moisture is driven out in order to avoid mechanical losses from material thrown out of the crucible by the rapid escape of steam and volatile matter.[a] This preliminary heating for four to six minutes is followed by the usual 7-minute application of the full flame.

[a] Lord, N. W., Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo. U. S. Geol. Survey Bull. 323 (reprinted as Bull. 28, Bureau of Mines), pp. 6-7.

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It should be clearly understood that the volatile matter does not represent any definite compound in the coal. The method of determination is wholly conventional, and any variation in temperature or rate of heating will change the amount of volatile matter determined.

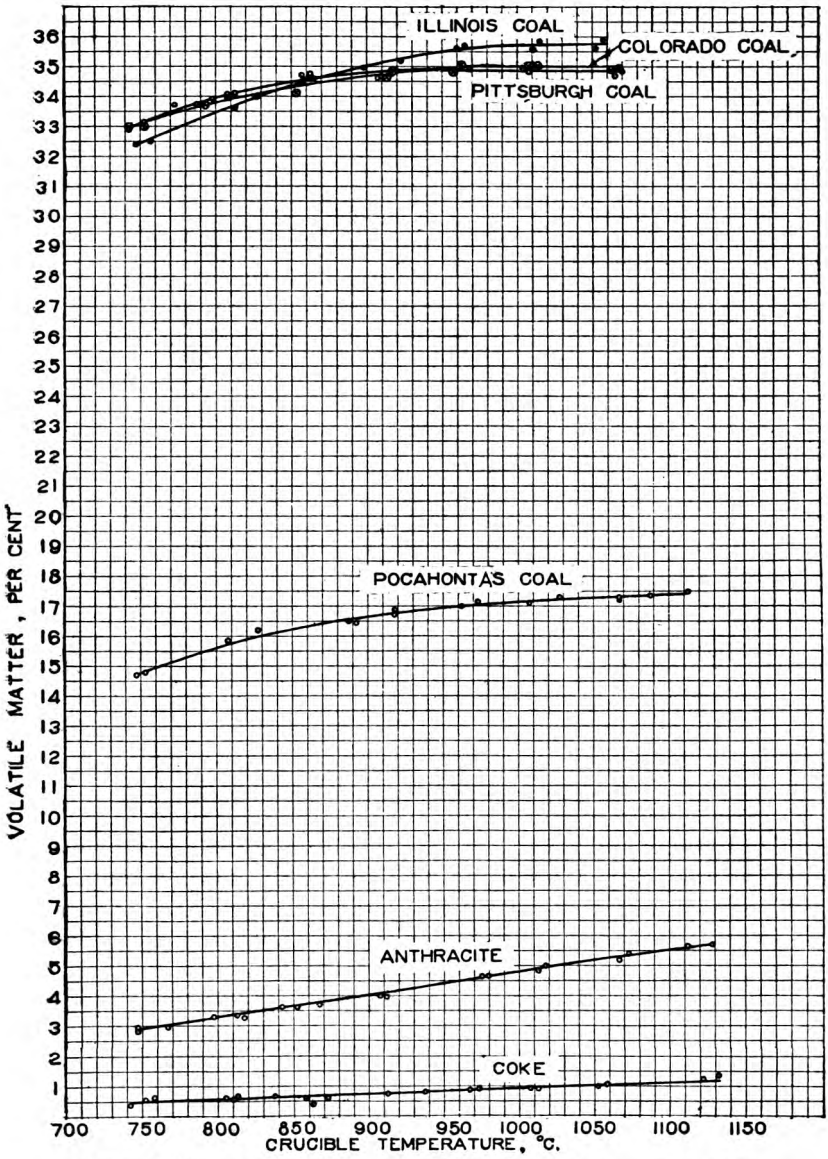

FIGURE 6.—Percentage of volatile matter from different coals at various temperatures.

This is graphically illustrated by the curves in figure 6, which represent the amount of volatile matter obtained by heating a number of portions of a single sample of coal at various temperatures between

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750° C. and 1,100° C.[a] This range of temperatures and consequent difference in volatile matter is quite likely to occur in different laboratories where different kinds of gas are used or where different gas pressures prevail, as shown by the experiments of Fieldner and Davis.[b] Coal gas and water gas will readily produce a crucible temperature of 950° C. when supplied to the burner at a pressure of about 2 inches of water, although changes in pressure will cause the temperature to fluctuate. Natural gas requires a larger proportion of air for complete combustion, and for this reason should be supplied at a pressure of not less than 10 inches of water to a good natural-gas burner of the Meker type, admitting ample air; otherwise the temperature in the crucible will be less than 950° C. The Meker burner, which has been used by the Bureau of Mines since July 1, 1911, is much superior to the Bunsen burner, especially for natural gas. The Meker construction practically eliminates the fluctuating inner cone of the ordinary Bunsen flame, and thus affords a solid flame of fairly uniform temperature, which completely envelops the bottom and sides of the crucible.

The 10-c. c. platinum crucible with capsule cover has been used for determinations of volatile matter at the Pittsburgh laboratory since November 1, 1912. The percentage of volatile matter obtained by the use of the 10-c. c. crucible is slightly lower than that obtained by the use of the 30-c. c. crucible formerly used. In a series of 58 different bituminous coals the average of the volatile matter obtained with the 10-c. c. crucible with capsule cover was 0.35 per cent less than the average obtained with the 30-c. c. crucible. In only 3 cases out of the 58 samples tested was the percentage of volatile matter obtained with the 10-c. c. crucible more than 1 per cent lower than that obtained with the 30-c. c. crucible.

In the determination of volatile matter in coke or anthracite with the ordinary 30-c. c. crucible with flat cover, the loss in weight due to oxidation often amounts to 1 per cent. This is due to the fact that there is not sufficient volatile matter in the sample to expel the 30 c. c. of air which is in the crucible when the heating is begun. The loss in weight of coke or anthracite by oxidation in the 10-c. c. crucible with capsule cover is usually less than 0.3 per cent.

The essential point in the determination of volatile matter is to adjust the heating apparatus to give a crucible temperature of 950° C. Heating in a burner flame has the advantage of surrounding the crucible with flame so that very little oxygen has access to the sample during the determination, thus reducing the oxida-

[a] Fieldner, A. C., and Hall, A. E., Influence of temperature on the determination of volatile matter in coal. Proc. 8th Intern. Cong. Appl. Chem., vol. 10, 1912, p. 139.

[b] Fieldner, A. C., and Davis, J. D., Some variations in the official method for the determination of volatile matter in coal. Jour. Ind. Eng. Chem., vol. 2, July, 1910, p. 304.

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tion. On the other hand, the flame temperature is difficult to control; variations in pressure and volume causing fluctuations in temperature.

If gas pressures fluctuate and a steady electric current is available, an electric furnace affords the most uniform means of heating. The additional oxidation due to the lack of flame protection is small (about 0.1 per cent), provided a 10-c. c. platinum crucible with close-fitting capsule cover is used.[a]

SULPHUR.

ESCHKA METHOD FOR DETERMINING SULPHUR.

Sulphur is determined by the Eschka method. "Eschka mixture" is made by thoroughly mixing light calcined magnesium oxide (MgO), two parts, with anhydrous sodium carbonate (Na_2CO_3) one part. A sample of 60-mesh coal weighing 1.3736 grams is thoroughly mixed in a 30-c. c. platinum or porcelain crucible with about 2 grams of Eschka mixture, and about 1 gram of Eschka mixture is spread over the top to form a cover. The crucible with its contents is placed on a triangle in a slanting position and the mixture is burned out over an alcohol, gasoline, or natural-gas flame. Artificial gas as a rule contains so much sulphur that its use may introduce an error in the determination, owing to the uncertainty regarding the quantity of sulphur taken up by the mixture. In starting the burning a very low flame must be used to avoid driving off volatile matter so fast that the sulphur escapes unburned. Even a small loss of sulphur dioxide (SO_2) may be detected by its pungent odor. The contents of the crucible should never be heated hot enough to cause the blackening of the Eschka-mixture cover.

After the crucible has been heated very slowly and cautiously for about 30 minutes the heat is increased, and after the crucible becomes red hot the contents are stirred occasionally until all black particles are burned out, a condition which indicates that the process is complete. The crucible and contents are then allowed to cool, and the contents are transferred to a 200-c. c. beaker and digested with 75 c. c. of hot water for at least 30 minutes. Filtration into a 300-c. c. beaker follows; the insoluble residue is washed twice with hot water by decantation, and after being transferred to the filter paper is washed with small quantities of hot water until the volume of solution in the 300-c. c. beaker is about 200 c. c. About 4 c. c. of saturated bromine water (or a slight excess) and enough concentrated hydrochloric acid (HCl) to make the solution slightly acid are added. The solution is next boiled, and the sulphur is precipitated as barium sulphate ($BaSO_4$) by adding 20 c. c. of a hot 5 per cent solution of

[a] Fieldner, A. C., and Hall, A. E., Influence of temperature on the determination of volatile matter in coal. Proc. 8th Intern. Cong. Appl. Chem., vol. 10, 1912, p. 148.

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barium chloride ($BaCl_2$). The solution containing the precipitate is allowed to stand for at least two hours at a temperature just below boiling. The following day it is filtered through an ashless filter paper and washed with pure hot water until a silver nitrate solution shows no precipitate with a drop of the filtrate. The test for excess barium chloride is made by adding a few drops of sulphuric acid solution to the filtrate. The precipitate is then ignited in a weighed porcelain crucible, free access of air being allowed and the paper being folded over the precipitate only loosely to prevent spattering. The paper should be smoked off very gradually at first, and the final heating should not be above a dull redness. After the paper is burned off completely the heating is continued for a few minutes, when the crucible is cooled and weighed. The weight in grams of barium sulphate after deducting the weight of barium sulphate found in a blank determination using the same reagents, multiplied by 10, equals the percentage of sulphur in the sample.

In routine analyses where a large number of determinations are made simultaneously the use of a muffle furnace heated electrically or by natural or gasoline gas is more convenient and rapid than heating over individual gas or alcohol burners. The crucibles containing the charge of coal and Eschka mixture are placed in the cold muffle, which is then gradually heated to a temperature of about 850° C. It should require at least 30 minutes to reach this temperature. The total time of heating is usually one and one-half to two hours. On removing the crucibles from the muffle the contents should be thoroughly stirred; if any black particles remain the crucibles should be returned to the muffle and heated until all black particles are burned.

DETERMINATION OF SULPHUR IN THE WASHINGS FROM A BOMB CALORIMETER.

After the combustion the calorimeter is washed out thoroughly and the washings collected in a 250-c. c. beaker. The washings are titrated with standard ammonia to obtain the "acid correction" for the heating value; 5 c. c. of dilute (1:2) hydrochloric acid is then added and the solution is heated to boiling. The insoluble matter is filtered off and washed five times with hot water. The filtrate and washings, which should have a total volume of 200 c. c., are heated to boiling and the sulphur is precipitated with barium chloride as described in the Eschka method.

$$\frac{\text{Weight of } BaSO_4 \times 13.74}{\text{Weight of sample}} = \text{percentage of sulphur.}$$

The results obtained by this method are usually somewhat lower (3 to 8 per cent of the total sulphur present) than are those obtained by the Eschka method. This is due to loss of sulphur trioxide in the gas escaping from the bomb and to retention of sulphur in the coal ash. However, the method has the advantage over the Eschka

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method of effecting a material saving in time. The results are sufficiently accurate for use in the purchase of fuel on a B. t. u. basis. This method is in use in the fuel-inspection laboratory of the Bureau of Mines.[a]

CARBON AND HYDROGEN.

METHOD WITH GAS-FIRED COMBUSTION FURNACE.

The determination of carbon and of hydrogen is made with a weighed quantity of sample in a 25-burner combustion furnace of the Glaser type. The products of combustion are thoroughly oxidized by being passed over red-hot copper oxide and lead chromate, and are fixed by absorbing the water in a weighed Marchand tube filled with granular calcium chloride ($CaCl_2$) and by absorbing the carbon dioxide in a Liebig bulb containing a 30 per cent solution of potassium hydroxide (KOH).

The apparatus used consists of a purifying train, in duplicate, a combustion tube in the furnace, and an absorption train. The purifying train consists of the following purifying reagents arranged in order of passage of air and oxygen through them: Sulphuric acid, potassium hydroxide solution, soda lime, and granular calcium chloride. One of the trains is for air and one for oxygen. In the sulphuric-acid and potassium-hydroxide scrubbing bottles the air and the oxygen are made to bubble through about 5 mm. of the purifying reagent. Both purifying trains are connected to the combustion tube by a Y tube, the joint being made tight by a rubber stopper.

The combustion tube is made of hard Jena glass. Its external diameter is about 21 mm., and its total length is 1 meter. The first 30 cm. of the tube is empty; following this empty space is an asbestos plug (acid washed and ignited) or in its place a roll of copper gauze may be used; the next 40 cm. is filled loosely with copper-oxide wire; a second asbestos plug separates the wire from 10 cm. of fused lead chromate, which is held in place by another asbestos plug 20 cm. from the end of the tube. The end of the tube is drawn out for rubber-tubing connection with the absorption train.

The absorption train consists, first, of a Marchand tube filled with granular calcium chloride ($CaCl_2$) to absorb moisture. This tube is followed by a Liebig bulb containing a 30 per cent potassium-hydroxide (KOH) solution, in which any possible impurities, as ferrous iron or nitrates, have been oxidized by a little potassium permanganate ($KMnO_4$). A guard tube, containing soda lime and granular calcium chloride, is attached to the Liebig bulb to absorb any carbon dioxide escaping the potassium-hydroxide solution and any water evaporating from that solution.

[a] See chapter on The fuel-inspection laboratory of the Bureau of Mines, by J. D. Davis, in Bull. 41, Bureau of Mines, p. 84.

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The train is connected to an aspirator which draws the products of combustion through the entire train. A guard tube of calcium chloride prevents moisture from running back into the absorption train. The suction is maintained constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. The connections are made as tight as possible. The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there are no more than three bubbles per minute in the potash bulb, the apparatus is considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, a blank is run by aspirating about 1 liter of air through the train, which is heated in the same manner as if a determination on coal were being made. If the Liebig bulb and the tube containing calcium chloride show a change in weight of less than 0.5 mg. each, the apparatus is in proper condition for use.

A 0.2-gram sample (crushed to 60-mesh) is weighed into a platinum or porcelain boat. The boat and sample are placed in a glass weighing tube closed with a stopper to prevent moisture changes. The absorption tubes are connected and the boat and sample are transferred from the weighing tube to the combustion tube, which should be cool for the first 30 cm. The copper oxide should be red hot and the lead chromate at a dull-red heat. The transfer of the boat from weighing tube to combustion tube should be made as rapidly as possible. As soon as the boat is in place (near the asbestos plug at the beginning of the copper oxide) the stopper connecting with the purifying train is inserted and the aspiration started with pure oxygen gas at the rate of three bubbles per second. One burner is turned on about 10 cm. back from the boat, and the aspiration is continued carefully until practically all the moisture is expelled from the sample. The heat is then increased very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back into the purifying train. The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited; then the temperature can be increased rapidly, but care should be taken not to melt the combustion tube. The aspiration with oxygen is continued for two minutes after the sample ceases to glow, the heat is then turned

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off and about 1,200 c. c. of air is aspirated. The absorption bulbs are then disconnected and weighed. The increase in weight of the calcium chloride tube times 55.55 equals the percentage of hydrogen. The increase in weight of the potassium hydroxide bulbs times 136.36 equals the percentage of carbon. The ash in the boat is weighed and carefully inspected for any unburned carbon which would destroy the value of the determination.

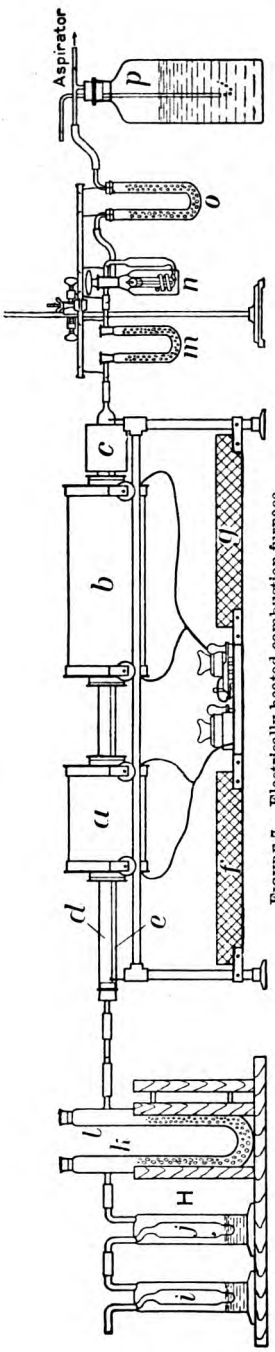

FIGURE 7.—Electrically heated combustion furnace.

METHOD WITH ELECTRICALLY HEATED COMBUSTION FURNACE.

The electrically heated combustion furnace used for the determination of hydrogen and carbon in fuels is of the Heraens type.

It consists of three independent heaters (*a*, *b*, and *c*, fig. 7); two of which, *a* and *b*, are provided with sheave wheels, and are mounted on a track so that they are movable along the tube; the third heater, *c*, which surrounds the lead chromate, is stationary.

The furnace as provided by the manufacturer does not include the small stationary heater. This was made in the laboratory by winding an alundum tube 12 cm. in length with No. 16 nichrome II wire and inclosing it in a cylinder packed with magnesia-asbestos. The movable heaters have very thin platinum foil, weighing about 9 grams in all, wound on a porcelain tube of 30 mm. internal diameter. The larger one, *b*, which heats the copper oxide, is 350 mm. in length, and the smaller one, *a*, which heats the sample in the boat, is 200 mm. in length. The Jena glass or fused silica combustion tube, *d*, of about 21 mm. external diameter and 900 mm. in length, is supported by an asbestos-lined nickel trough, *e*. The current through each heater is regulated independently by separate rheostats, *f*, *g*, mounted on the frame of the furnace. The two platinum-wound heaters require an average current of about 4.5 amperes at a pressure of 220 volts, although for heating rapidly a larger amperage is necessary.

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The oxygen or air entering the combustion tube is purified by passing through a Tauber's drying apparatus, H, which contains the following reagents arranged in order of the passage of air or oxygen through them: Sulphuric acid, *i*, for removing possible traces of ammonia, 30 per cent potassium hydroxide (KOH) solution, *j*, granular soda lime, *k*, and granular calcium chloride, *l*. One side of the train is connected directly to a Linde oxygen tank, which is provided with a reducing valve for regulating the oxygen pressure; the other side of the train is used for purifying the air supply.

The absorption train consists of a 5-inch U tube, *m*, filled with granular calcium chloride ($CaCl_2$) to absorb moisture. Before using, the calcium chloride should be saturated with carbon dioxide to avoid possible absorption of carbon dioxide during a determination by any traces of calcium oxide that may be present. This saturating is done most conveniently by placing a quantity of calcium chloride in a large drying jar, and filling the jar with carbon dioxide. After standing over night, dry air is drawn through the jar to remove the carbon dioxide. The treated calcium chloride is kept in well-stoppered bottles.

The calcium chloride tube is connected to a Vanier potash bulb, *n*, containing a 30 per cent potassium hydroxide solution and granular calcium chloride. Six to eight determinations can be made without recharging this bulb. The potash bulb is connected to an aspirator through a guard tube, *o*, containing granular calcium chloride and soda lime, and a Mariotte flask, *p*. The Mariotte flask keeps the pressure constant.

In general, the method of determination is the same as the one used with the gas furnace. By moving the heaters toward the end of the tube where the gases enter, and cutting in the electric current, the air can be warmed enough to thoroughly dry the tube and its contents. The current is then cut off from the small heater, *a*, and the large heater, *b*, is moved over the copper oxide; about 250 mm. of that part of the combustion tube between the two heaters where the boat containing the sample is to be placed is kept exposed. The full current is then turned on the large heater to bring the copper oxide to a red heat. When this temperature is reached it is necessary to reduce the current with the rheostat to avoid melting the tube. In the meantime the absorption train is weighed and connected, and the boat containing the sample is placed in the exposed and cooler part of the tube between the two heaters.

The current is then passed through the shorter heater. By manipulating the rheostat and by gradually pushing this heater toward the boat, the rate of evaporation of moisture and evolution of volatile matter can be readily controlled.

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After combustion is complete, the electric current is turned off the smaller heater and this heater moved back to allow the tube to cool for the next determination. The final aspiration of air and the weighing of the absorption train is conducted as described under the gas-furnace method.

NITROGEN.

The well-known Kjeldahl-gunning method is used in determining nitrogen. One gram of the coal sample is boiled with 30 c. c. of concentrated sulphuric acid (H_2SO_4), 5 grams of potassium sulphate (K_2SO_4), and 0.6 gram of mercury in a 500-c. c. Kjeldahl flask until all particles of coal are oxidized and the solution nearly colorless. The boiling should be continued at least two hours after the solution has reached the straw-colored stage. A few crystals of potassium permanganate ($KMnO_4$) added, after digesting a few hours, will aid in reducing the time of boiling required for the oxidation of coke and anthracite. After cooling, the solution is diluted to about 200 c. c. with cold water. Twenty-five cubic centimeters of potassium sulphide (K_2S) solution (40 grams K_2S per liter) is added to precipitate the mercury, and 1 to 2 grams of granular zinc to prevent bumping. Enough saturated sodium hydroxide (NaOH) solution (usually 80 to 100 c. c.) to make the solution distinctly alkaline is gradually added and the flask is at once connected with the condenser.

The danger of loss of ammonia may be minimized by holding the flask in an inclined position while the sodium hydroxide solution is being added. The alkaline solution runs down the side of the flask and forms a layer below the lighter acid solution. After the flask is connected to the condensing apparatus the solution is mixed by gently shaking the flask.

The ammonia (NH_3) is distilled over into a measured amount (10 c. c.) of standard sulphuric acid solution, to which has been added sufficient cochineal indicator for titration. The solution is distilled until about 200 c. c. of distillate has passed over, and the distillate is titrated with standard ammonia (NH_4OH) solution (20 c. c. NH_4OH solution = 10 c. c. H_2SO_4 solution = 0.05 gram nitrogen).

The transfer to a distillation flask may be avoided by the use of a 500-c. c. Kjeldahl flask for digestion of the coal, connection being made direct from the Kjeldahl digestion flask to the condensing apparatus.

In routine work the determinations are made in sets of 12, the digesting and distilling apparatus being designed for 12 flasks. One flask in each set contains a blank determination in which 1 gram of pure sucrose (cane sugar) is substituted in place of the usual coal sample. The nitrogen found in this blank determination is deducted

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from the nitrogen found in each of the 11 determinations that were made in the same set.

Usually the sodium hydroxide and potassium sulphide are dissolved in a single stock solution. A 25-pound drum of electrolytic caustic soda is dissolved in 18 liters of water, contained in a six-gallon stoneware jar. Potassium sulphide is then added until the quantity of alkali solution necessary for a nitrogen determination (85 to 100 c. c.) contains 1 gram of potassium sulphide. The above proportions, caustic soda 99 per cent pure being used, require 280 grams of potassium sulphide.

PHOSPHORUS.

For the determination of phosphorus in coal or coke, a sample weighing 6.52 grams is burned to ash in the muffle furnace. The ash is mixed with four to six times its weight of sodium carbonate plus 0.2 gram of sodium nitrate, and is fused at the highest temperature of the blast lamp. The fused mass is dissolved in water, acidified, and evaporated to dryness. The residue is taken up in hydrochloric acid, and the phosphorus determined in the usual way, either by weighing or by titrating the yellow precipitate with permanganate.

DETERMINATION OF PHOSPHORUS IN COKE.

The following method, recommended by a committee of the American Foundrymen's Association,[a] has given excellent results:

Ignite 5 grams of coke in a platinum dish or large platinum crucible until all the carbon is burned off. Add 10 c. c. of dilute hydrochloric acid (1:1) and 20 c. c. of hydrofluoric acid, evaporate to dryness, and ignite at a dull-red heat. Fuse the residue with about 3 grams of sodium carbonate and 0.3 gram of potassium nitrate, cool, place the dish containing the fusion in a beaker of water, and boil. When the fusion is completely dissolved rinse the dish into the solution and lay aside. Acidify the solution with hydrochloric acid, precipitate with ammonia, boil, filter, and wash with hot water. Wash the filter with warm dilute nitric acid to dissolve the precipitate. Should it not dissolve, wash it with warm dilute hydrochloric acid until it is dissolved. In the latter case it is necessary to evaporate the solution to a volume of about 5 c. c.; add 30 c. c. of nitric acid (1.20 sp. gr.); again evaporate to about 5 c. c. and add 30 c. c. of nitric acid (1.20 sp. gr.). After heating the solution to between 70° and 90° C., add 50 c. c. of molybdate solution. Stir the solution a few minutes, then filter; wash five times with a 3 per cent nitric acid solution and five times with a 0.1 per cent potassium nitrate solution. Transfer the precipitate and filter to the flask in which the precipitate

[a] Transactions of American Foundrymen's Association, vol. 20, 1912, p. 561.

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was made. Add 30 c. c. of water, then $\frac{N}{5}$ sodium hydroxide from a burette until in excess, keeping the solution agitated. When the yellow precipitate is all dissolved, add 0.1 c. c. of phenolphthalein solution as an indicator, and then titrate with $\frac{N}{5}$ sulphuric acid.

$$\text{C. c. } \tfrac{N}{5}\text{NaOH} = \text{c. c. } \tfrac{N}{5}\ H_2SO_4 \times .0054 = \text{percentage of phosphorus.}$$

To make the molybdate solution, add 100 grams of molybdic acid to 250 c. c. of water and to this add 150 c. c. of ammonia. Stir until all is dissolved and then add 65 c. c. of nitric acid (1.42 sp. gr.). Make another solution by adding 400 c. c. of concentrated nitric acid to 1,100 c. c. of water. When the solutions are cool, pour the first solution slowly into the second, stirring constantly, and add a couple of drops of ammonium phosphate.

DETERMINATION OF THE CALORIFIC VALUE OF COAL.

Determination of the calorific value of coal is made with the bomb calorimeter. The method used is applicable to the Mahler, Atwater, Williams, and Emerson bomb calorimeters, all of which are in use in the laboratories of the bureau. The following is a brief description of the details of operation:

A 1-gram sample of coal (60-mesh) is placed in a platinum tray, the bottom of which is covered with a piece of asbestos paper that has been washed and ignited. The use of this asbestos mat avoids trouble in completely burning anthracite coal. One of the platinum terminals of the firing circuit is attached to the tray. The terminals are connected by a piece of iron wire (platinum wires should be used when the bomb is platinum-lined) 105 mm. long, 0.16 mm. in diameter, and weighing about 13 mg. The ends of the wire are attached to the platinum terminals, which must be clean, simply by wrapping the wire tightly around them. The iron wire is bent down so as to touch the coal sample on the mat within the tray. The tray is then placed in the bomb and the lid screwed down tightly against the lead gasket. Oxygen is forced into the bomb until the manometer recording the pressure within the bomb reads 18 to 20 atmospheres, when the needle-point valve is closed just tight enough to prevent leakage of gas. The oxygen must be admitted very slowly to avoid blowing any particles of coal dust out of the tray. With some extremely light materials, such as peat, it is best to briquet the sample and take a weighed portion of the broken briquets instead of using the powdered sample.

The bomb filled with oxygen is placed in the brass bucket containing 2,000 to 2,500 grams of distilled water, depending upon the

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type of calorimeter used, the bucket having been previously placed in the insulated jacket. The temperature of the water should be from 2.5° to 3° C. below the temperature of the water jacket. The stirring apparatus is adjusted so that it touches neither bucket nor bomb, and the thermometer is inserted so that the bulb is about 5 cm. from the bottom of the bucket and is in contact with no metal parts of the apparatus. The outside terminals of the bomb are connected with wires leading to the switch. After the stirrer has been in motion for about a minute, or when the water has been thoroughly mixed, the first reading of the thermometer is taken by means of a reading telescope attached to a cathetometer. The thermometer is graduated to 0.01° C., and the readings can be interpolated to 0.001° C. For accurate calorimetric work the thermometers should be calibrated to 0.001° C. The stirring should be continued at a uniform rate throughout the determination, and should be sufficiently rapid to insure thorough mixing. In covered calorimeters the temperature should never be allowed to rise more than 1° C. above the temperature of the water jacket.

A reading telescope and cathetometer greatly improve the accuracy of the thermometer readings.

The instrument shown in figure 8 was built in the machine shop of the bureau.

The sliding carriage *a* moves freely on the brass tube *b* inside of which is a lead counterweight, *c*.

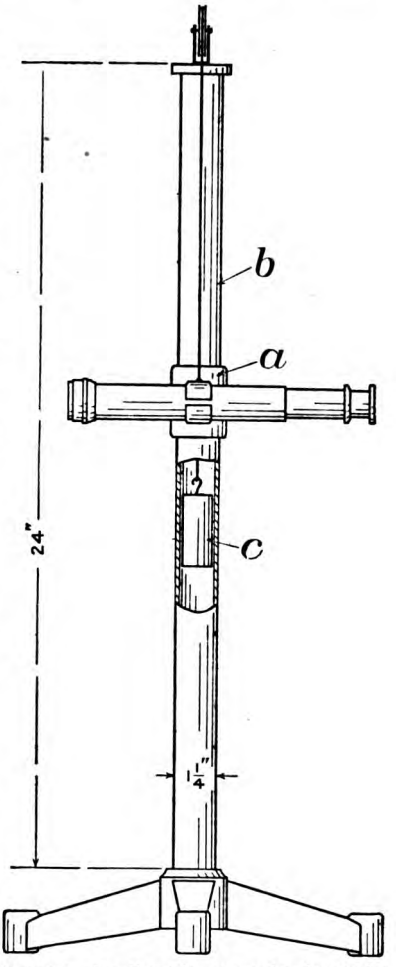

FIGURE 8.—Reading telescope and cathetometer.

The reading telescope, which has a magnifying power of 55 diameters, may be adjusted at any angle with the horizontal, to suit the convenience of the operator; however, this angle must be maintained constant throughout a determination.

Rotation of the telescope around the tube is prevented by a projecting pin in the carriage, which engages a vertical groove in the brass tube.

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The actual determination may be divided into three periods—the preliminary period, the combustion period, and the final period. The preliminary period usually requires five readings taken one minute apart, or until the rate of change per minute is nearly constant. After taking the fifth reading the current at 20 volts is turned on for about one-half second. This is the beginning of the combustion period. The first two readings in this period are taken one-half minute apart because the change in temperature is so great. The temperature rises to a maximum and then begins to fall; after its rate of fall becomes uniform, readings are taken every minute for five or six minutes. The final reading of the combustion period is the first reading after the rate of fall becomes uniform.

The following figures are from an actual determination and show the method of calculating the result, and the corrections applied:

Method of calculating from calorimeter readings.

[Sample No. 10743. Weight 1.0000 gram.]

Time, p. m.	Readings, °C.			
1.00				
.54	23.874	.0058	rate of change in preliminary period.	26.463
.55	23.879			23.897
.56	23.885		Observed temperature change	2.566
.57	23.892		Thermometer correction	.002
			Stem correction	.000
.58	23.897	+[a].0058		2.564
		+[b].0027	Radiation loss	.0066
				2.5706
.58½	24.160	+[a].0049	Water equivalent	3000
		+[b].0014		
.59	25.430	+[a].0008	Total heat developed.....(calories)..	7,711.8
		−[b].0006	Correction	40.3
.60	26.280	−[a].0020	Heat developed by combustion of sample.....(calories)..	7,671.5
		−[b].0023		
2.01	26.439	−[a].0025		
		−[b].0026		
.02	26.463	−[a].0026		
		−[b].0026		
.03	26.466	−[a].0026		
		−[b].0026		
		−.0066	algebraic sum.	
.04	26.463			
.05	26.460			
.06	26.458	−.0026	rate of change in final period.	
.07	26.455			
.08	26.454			
.09	26.450			

	Calories.
Wire burned=11.2 mg.	=17.9
Titer (1 c. c. =5 cal.), 2.5 c. c.	=12.5
Sulphur (0.01 gm.=13 cal.), 0.0076 gm.	= 9.9
Room temperature=24°C.	40.3

[a] Computed rate per minute of temperature change at each reading.

[b] Temperature correction for heat loss during each interval.

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The reading 23.874°, taken at 1.54 p. m., is the first reading of the preliminary period. The temperature reading 23.897° is the last reading of the preliminary period and was taken at 1.58 p. m., 4 minutes after the first reading; hence $23.897° - 23.874° = 0.023°$, total change in temperature during the preliminary period; also $0.023° \div 4 = 0.0058°$, rate of change per minute during the preliminary period.

The rate of change per minute in the final period is found in like manner to be $-0.0026°$; hence $+0.0058° - (-0.0026°) = 0.0084°$, change in rate during the combustion period.

The observed change in temperature during the combustion period is 2.564°; the change in rate per degree of temperature change in the combustion period is therefore equal to $\frac{0.0084°}{2.564°} = 0.0033°$.

The change in temperature during the first half minute of the combustion period is 0.263°, and

$0.263° \times 0.0033° = .0009°$, change in rate during first half minute of combustion period.

$0.0058° - 0.0009° = .0049°$, rate of temperature change at reading at $1.58\frac{1}{2}$ p. m.

The rate of change for each succeeding reading in the combustion period is calculated in the same way.

The temperature correction for the heat loss during the half-minute readings is made by dividing the algebraic sum of the rates by 4, and for the minute readings the algebraic sum is divided by 2, because the temperature correction for heat loss during each interval is the mean rate per minute of temperature change multiplied by the time of the interval in minutes. For example, at 1.58 p. m. the rate per minute of temperature change is +0.0058°, and at $1.58\frac{1}{2}$ the rate per minute of temperature change is +0.0049°; therefore the mean rate per minute of temperature change for the one-half minute interval is $\frac{0.0058 + (+0.0049)}{2} = +0.0054°$, and $\frac{1}{2} \times (+0.0054) = +0.0027$, which is the correction for heat loss taking place during the half-minute interval. The algebraic sum of all the temperature corrections for heat loss during each interval is added to the observed temperature change after corrections have been made for the errors and stem correction in the thermometer; this figure multiplied by the water equivalent of the apparatus gives the total heat developed.

By the use of a slide rule the analyst can easily compute a calorimeter determination while making the observations of the following determination.

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DERIVATION OF FORMULA USED.

The above method of calculating the radiation loss may be reduced to a formula derived by Lawrence Griffin under the direction of Lauson Stone, engineer, of the Bureau of Mines. This formula, which is especially adapted for calculation with computing machines of the "Comptometer" type, is derived as follows:

Observations of time and temperature.

Time, p. m.		Readings, degrees centigrade.
1.54 to 1.58	Preliminary period	B
.58½		a
.59		b
.60		c
2.01		d
.02		e
.03 to 2.09	Final period	A

C=rate of change in preliminary period.

D=rate of change in final period.

Change of temperature during combustion period=A−B.

Change of rate of radiation per degree of temperature change in combustion period=$\frac{C-D}{A-B}$=K.

Change of temperature during last minute of combustion period=A−e.

Therefore:

Change in "rate of radiation" during last minute=(A−e)K; in the last two minutes=(A−d)K; in the last 3 minutes=(A−c)K; in the last 4 minutes=(A−b)K; in the last 4½ minutes=(A−a)K; in the last 5 minutes=(A−B)K.

So the "rate of temperature change" for each reading is as follows:

Rate of change of temperature.

Time, p. m.	Readings, degrees centigrade.	Rate of change.
1.58	B	D+(A−B)K=C
.58½	a	D+(A−a)K
.59	b	D+(A−b)K
.60	c	D+(A−c)K
2.01	d	D+(A−d)K
2.02	e	D+(A−e)K
2.03	A	D

Temperature correction for heat loss for the half-minute periods is made by dividing the sum of the rates by 4, and for the minute periods by dividing the sum of the rates by 2, thus:

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$$\left[\frac{D+(A-B)K+D+(A-a)K}{4}\right]$$
$$\left[\frac{D+(A-a)K+D+(A-b)K}{4}\right]$$
$$\left[\frac{D+(A-b)K+D+(A-c)K}{2}\right]$$
$$\left[\frac{D+(A-c)K+D+(A-d)K}{2}\right]$$
$$\left[\frac{D+(A-d)K+D+(A-e)K}{2}\right]$$
$$\left[\frac{D+(A-e)K+D}{2}\right]$$

The above quantities reduce to—

$$\left[\frac{D-\left(\frac{B}{2}+\frac{a}{2}-A\right)K}{2}\right]$$
$$\left[\frac{D-\left(\frac{a}{2}+\frac{b}{2}-A\right)K}{2}\right]$$
$$\left[\frac{2D-(b+c-2A)K}{2}\right]$$
$$\left[\frac{2D-(c+d-2A)K}{2}\right]$$
$$\left[\frac{2D-(d+e-2A)K}{2}\right]$$
$$\left[\frac{2D-(e-A)K}{2}\right]$$

By adding these quantities we get the temperature correction for the heat lost during the combustion period. The sum appears as follows:

$$\tfrac{1}{2}\left[10D-\left(\frac{B}{2}+a+\frac{3b}{2}+2c+2d+2e-9A\right)K\right]$$

or

$$5D-\left[\left(\frac{B}{4}+\frac{a}{2}+\frac{3b}{4}+c+d+e-\frac{9A}{2}\right)\right]K$$

Let n equal the number of readings during the combustion period. It will be observed that the coefficient of D is $(n-2)$ and that of A is $\left(n-\frac{5}{2}\right)$, a relation which holds for all cases of two readings one-half minute apart at the beginning of the combustion period.

The formula now may be stated as:

$$(n-2)D-\left[\frac{B}{4}+\frac{a}{2}+\frac{3b}{4}+c+d\ldots\ldots-\left(n-\frac{5A}{2}\right)\right]K \qquad (1)$$

For cases of four readings one-half minute apart at the beginning of the combustion period, the formula becomes:

$$(n-3)D-\left[\frac{B}{4}+\frac{a}{2}+\frac{b}{2}+\frac{c}{2}+\frac{3d}{4}+e+f+\ldots\ldots-\left(n-\frac{7A}{2}\right)\right]K \qquad (2)$$

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APPLICATION OF FORMULA.

For two one-half minute readings formula 1 is applied as follows:

Application of first formula for radiation loss.

Time, p. m.	Readings, ° C.		
1.58	23.897 (B)	+.0058 (C)	$\frac{C-D}{A-B}=\frac{.0084}{2.566}=K$
.58½	24.160 (a)		
.59	25.430 (b)		
.60	26.280 (c)		n=8
2.01	26.439 (d)		
.02	26.463 (e)		$\frac{B}{4}=5.974$
.03	26.466 (f)		
.04	26.463 (A)	$-\frac{.0026(D)}{.0084}$	
			$\frac{a}{2}=12.080$
			$\frac{3b}{4}=19.072$
		c+d+.....=	105.648
		Sum=	142.774
		$\frac{11A}{2}=-$	145.546
		−	2.772
		$-2.772\times\frac{.0084}{2.566}=$ −	.0091
		6D=−	.0156
		Radiation loss =−	.0156−(−.0091)=.0065

Further corrections must be deducted for heat due to formation of aqueous nitric acid and sulphuric acid and to combustion of the iron wire. The correction for iron wire is 1.6 calories per milligram. The correction for sulphur burned to sulphuric acid (H_2SO_4) is 13 calories per 0.01 gram of sulphur. The correction for nitrogen to aqueous nitric acid is made by titrating the acidity of the bomb liquor with standard ammonia solution (0.00587 gram NH_3 per c. c.), and is equivalent to 5 calories per cubic centimeter.

DETERMINATION OF SULPHUR—CORRECTION FOR ACIDITY.

After the combustion of the coal in the calorimeter the bomb is washed out thoroughly and the washings are titrated with standard ammonia solution (0.00587 gram per c. c.), methyl orange being used as an indicator. The acidity is due to the nitric acid (HNO_3) formed from the nitrogen of the coal and the nitrogen of the air in the bomb, and also to the sulphuric acid (H_2SO_4) formed from the combustion of the sulphur in the coal. The sulphur can be easily determined by precipitation as barium sulphate ($BaSO_4$). It is convenient to make the ammonia solution of such strength that 1 c. c. is equivalent to 0.00483 gram of nitrogen, for this weight of nitrogen burned to nitrogen pentoxide (N_2O_5) plus water generates 5 calories of heat. The figures are derived as follows:

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The calorific value of nitrogen burning to N_2O_5 + water is 1,035 calories per gram.

1,035 calories : 5 calories : : 1 gram : 0.00483 gram.

Therefore 0.00483 gram of nitrogen generates 5 calories of heat when burned to aqueous nitric acid.

The ammonia solution is made up according to the equation

$$HNO_3+NH_3=NH_4NO_3.$$

Since N = 14, and $NH_3 = 17$,

$$14 : 17 = 0.00483 \text{ gram} : 0.00587 \text{ gram}.$$

Therefore 0.00587 gram of NH_3 is equivalent to 0.00483 gram of nitrogen, which when burned to aqueous nitric acid (HNO_3) generates 5 calories of heat. The standard solution contains 5.87 grams of NH_3 per liter. The solution, when used to titrate the bomb liquor after combustion of a coal sample, must satisfy not only the nitric acid formed but also any sulphuric acid resulting from the combustion of the sulphur in the coal.

The strength of the ammonia solution in terms of sulphur in the form of sulphuric acid (H_2SO_4) is determined by the following equation:

$$2NH_3+H_2SO_4=(NH_4)_2SO_4$$

$$2NH_3 : S = 34 : 32 = 0.00587 \text{ gram } NH_3 : 0.0055 \text{ gram S}.$$

The heat of combustion of sulphur to aqueous sulphuric acid (H_2SO_4) is 4,450 calories per gram of sulphur. This reaction takes place in the bomb calorimeter when the fuel is burned in an atmosphere of oxygen under high pressure.

In the ordinary combustion of coal under a boiler the sulphur burns to sulphur dioxide (SO_2), the heat of formation of which is 2,250 calories per gram of sulphur. The difference between these two calorific values (4,450 calories − 2,250 calories) is 2,200 calories per gram of sulphur. Therefore it is necessary to make a correction of 2,200 calories per gram of sulphur in the calorimeter determinations, owing to the formation of aqueous sulphuric acid. Since 1 c. c. of the ammonia solution is equivalent to 0.0055 gram of sulphur, 0.0055 times 2,200 equals 12.1 calories, the heat correction to be made if all the acidity of the liquor from the bomb represented sulphuric acid (H_2SO_4).

Hence the ammonia solution containing 0.00587 gram (NH_3) per cubic centimeter is equivalent to 5 calories for nitrogen converted to aqueous nitric acid (HNO_3), or to 12.1 calories for sulphur converted to aqueous sulphuric acid (H_2SO_4). A further correction, therefore, must be applied for the sulphur that is determined separately. This correction is a function of the difference between the value of the ammonia solution in terms of sulphur (12.1 calories) and its value in

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terms of nitrogen (5 calories), or 7.1 calories. The difference, 7.1, divided by 0.0055, the value of 1 c. c. of ammonia solution in grams of sulphur, equals 1,291 calories per gram of sulphur, or 13 calories for each 0.01 gram of sulphur.

The total acidity correction is, then, the cubic centimeters of ammonia (NH_3) solution multiplied by 5 (the factor for nitric acid) plus the centigrams of sulphur multiplied by 13.

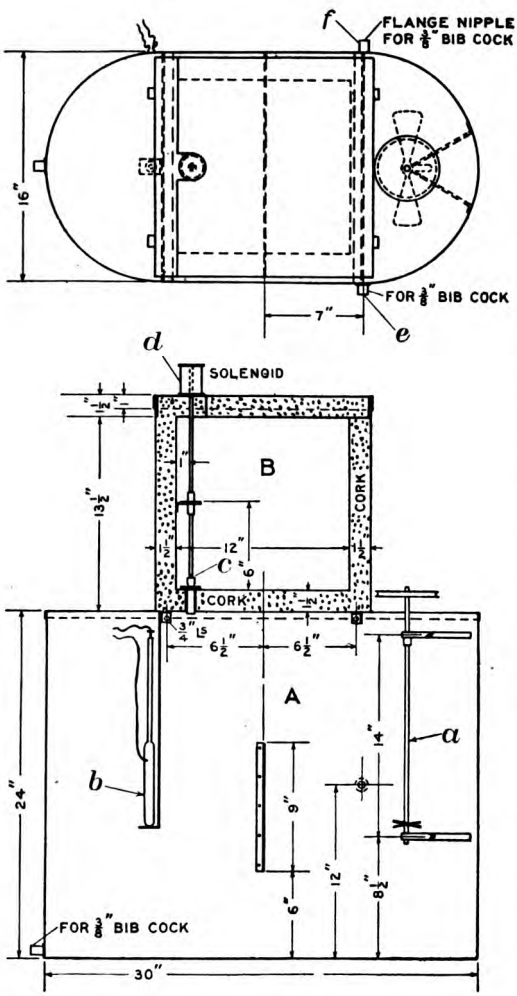

FIGURE 9.—Constant-temperature apparatus.

CONSTANT-TEMPERATURE TANK FOR CALORIMETER WATER.

A constant-temperature apparatus (shown in fig. 9) provides a supply of water at the proper starting temperature for calorimetric determinations. This apparatus consists of a large copper tank, A, containing a stirrer, *a*, driven by a small electric motor, and an electric thermostat, *b*, which operates an electromagnetic valve, *c*, in the ice-water tank B. After a calorimetric determination has been made, the slightly warmed water in the bucket is returned to the large tank. The addition of this warmer water causes the thermostat to close an electrical circuit through a dry battery and relay, which in turn closes a 220-volt circuit through the coil of the electromagnet *d*, which opens the valve admitting ice water. When the water in the large tank has cooled to the proper temperature, the circuit is automatically broken and the valve closes. The water for each determination is drawn off from the tank at the cocks *e* and *f*, and is weighed in the calorimeter bucket. A tare weight equal to the total water equivalent of the calorimeter plus the weight of the empty bucket is provided by means of a strong glass bottle containing shot.

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STANDARDIZATION OF THE CALORIMETER.

The first detail to be considered in calorimetric work is the correct determination of the water-equivalent value of the apparatus. This equivalent may be determined by a number of methods, which differ in accuracy, as follows:

1. By adding the products of the weight of the different parts of the apparatus times their specific heat.
2. By generating heat within the bomb by passing a measured electric current through a known resistance for a given length of time.
3. By adding definite weights of water at different temperatures to the system and noting the corresponding temperature changes.
4. By varying the quantity of water surrounding the bomb, thus keeping the heat generated within the bomb constant.
5. By the combustion of a substance of known calorific value.

METHOD OF SPECIFIC HEATS.

One of the Mahler bombs (No. 411) of the Bureau of Mines showed a water equivalent of 500 as determined from the average of 15 combustions of pure naphthalene, benzoic acid, and sucrose (cane sugar); this value was checked by the method of specific heats with the following results:

Determination of water equivalent by method of specific heats.

	Weight, grams.	Specific heat.	Water equivalent.
Steel (bomb)	3,946.4 ×	[a] 0.1097 =	432.92
Brass (bucket)	732.9 ×	[a] 0.093 =	68.16
Lead (gasket), mercury (thermometer), platinum (tray and supports)	81.6 ×	[a] 0.0324 =	2.64
Enamel (lining of bomb)	20.0 ×	[b] 0.2045 =	4.09
Glass (immersed portion of thermometer)	11.5 ×	[c] 0.1988 =	2.29
Oxygen (in bomb)	14.0 ×	[c] 0.2175 =	3.05
Water (in bomb)	3.0 ×	1 =	3.00
			516.15

The standardization of a bomb calorimeter by the above method is not satisfactory. It is usually impossible to weigh each part of the bomb. For instance, in the Mahler bomb the weight of the porcelain lining can be estimated only; furthermore, there is no accurate method of allowing for the portions of the bomb, bucket, and stirrer that are not immersed in the water.

[a] Stohman. [b] Louguinine. [c] Landolt and Börnstein.

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ELECTRICAL METHOD.

The electrical method [a] of standardization is capable of the highest degree of accuracy, and is used for fundamental determinations of the heating values of standard substances, such as sucrose, benzoic acid, and naphthalene. However, the accurately calibrated and necessarily expensive electrical measuring instruments required by this method place it beyond the reach of the average technical laboratory.

METHOD OF MIXTURES.

The method of mixtures [b] has been widely used in the standardization of calorimeters. A serious objection against the use of this method is the experimental difficulty of determining the exact temperature at which the warmer or colder water is introduced. Furthermore, the conditions of standardization differ from those prevailing during an actual combustion, so that uncertainties in the correction for "heat losses" are introduced.

DIFFERENTIAL METHOD.

The water equivalent of the ordinary type of bomb calorimeter can not be determined accurately by varying the quantity of water in the calorimeter bucket, as a variation of water level changes the heat capacity of the instrument; also, the comparatively small differences in quantity of water that must necessarily be used greatly multiply the chances of thermometric errors.[c]

METHOD OF KNOWN CALORIFIC VALUES.

The most convenient and accurate method of calibrating commercial calorimeters is by the combustion of standard substances the calorific values of which have been accurately determined in calorimeters calibrated by electrical methods. Standard substances of certified calorific value may now be obtained from the Bureau of Standards,[d] as follows:

Calorific value of standard substances.

	Calories.[e]
Benzoic acid	6,320
Naphthalene	9,610
Sucrose	3,945

In using this method the final water-equivalent value should be based on an average of at least five determinations, which should be carried out with the thermometer used in daily work and under the

[a] Jaeger, W., and Steinwehr, H. v., Ann. Phys., vol. 21, 1906, pp. 23–63; also Bulletin of the Bureau of Standards, Reprint 135. 1909.

[b] For details of this method as applied by E. E. Somermeier see Coal, by Bownocker, Lord, and Somermeier, Geol. Surv. Ohio, Bull. 9, 1908, p. 331.

[c] Bownocker, J. A., Lord, N. W., and Somermeier, E. E., Coal, Bull. 9, Geol. Surv. Ohio, 1908, pp. 332–334.

[d] Bureau of Standards, Circular 11, The standardization of bomb calorimeters. 1911. 10 pp.

[e] For 1 gram of substance weighed in air.

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same conditions that prevail in the routine operation of the apparatus. The weight of substance taken for a combustion should give approximately the same rise of temperature as is obtained in the combustion of 1 gram of coal; for naphthalene this weight is about 0.8 gram; benzoic acid, 1.2 grams; sucrose, 2 grams.

The charge should be made into a briquet and, as soon as weighed, should be placed in the bomb. The determination of calorific value is made in the same manner as described for coal. Corrections for "radiation," thermometer, iron wire, and acidity are made as shown on page 28. After the corrected change of temperature (2.5706 in the specimen calorimeter determination on p. 28) has been obtained, the water equivalent is completed by the following formula:

$$E=\frac{HW+C}{T}$$

in which

E=water equivalent of calorimeter.
H=heat of combustion of 1 gram of the standard substance.
W=weight in grams of sample taken.
C=correction for iron fuse wire burned and heat from formation of nitric acid.
T=change of temperature, corrected for radiation and thermometric errors.

A Mahler bomb calorimeter which was standardized by the combustion of naphthalene, benzoic acid, and sucrose gave the following concordant results:

Four determinations with naphthalene, calorific value 9,610, gave water-equivalent values of 2,996, 2,993, 2,999, and 2,994 grams; average, 2,995 grams.

Five determinations with benzoic acid, calorific value 6,320, gave water-equivalent values of 2,994, 3,002, 2,989, 2,994, and 2,992 grams; average, 2,994 grams.

Five determinations with sucrose, calorific value 3,945, gave water-equivalent values of 2,993, 2,993, 2,996, 2,994, and 2,994 grams; average, 2,994 grams.

DETERMINATION OF THE TRUE SPECIFIC GRAVITY OF COAL AND COKE SUBSTANCE.

ORDINARY METHOD.

To determine the true specific gravity of coal and coke substance, the procedure is as follows: Approximately 3.5 grams of the 60-mesh coal or coke is weighed and introduced into a 50-c. c. pycnometer with about 30 c. c. of distilled water. In order to avoid loss of particles of the sample during boiling, a one-bulb, 6-inch drying tube (*a*, fig. 10) is connected with the pycnometer by means of a small piece of pure gum tubing, *c*. The other end of the drying tube is connected with

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the aspirator. Suction is applied and the contents of the flask are gently boiled on the water bath *d* under partial vacuum for three hours in order to expel all air from the sample. The pycnometer is then detached, almost filled with boiled and cooled water, allowed to cool to the temperature of the balance room, stoppered, and weighed. The temperature of the contents of the pycnometer is taken immediately after weighing. Each pycnometer is accurately calibrated and a table is constructed giving its capacity in grams of water at different temperatures.

The true specific gravity is determined by use of the following formula:

$$\text{True specific gravity} = \frac{W}{W-(W'-P)}$$

in which

W = weight in grams of dry coke = weight in grams of sample − its moisture content.

W′ = weight in grams of pycnometer + dry coke + water to fill.

P = weight in grams of pycnometer + water to fill.

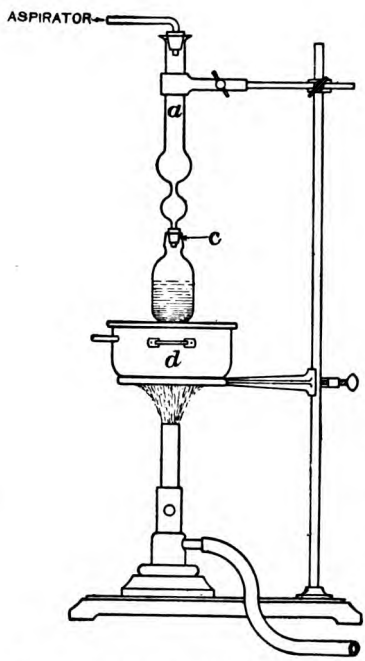

FIGURE 10.—Arrangement of pycnometer.

SPECIAL METHOD.

The Hogarth flask recommended by Blair[a] for the determination of the specific gravity of iron ores is more convenient and accurate for routine determinations of the specific gravity of coal or coke substances than is the ordinary pycnometer described in the preceding method. With the ordinary pycnometer it is difficult to insert the stopper without catching some floating particles between the stopper and neck.

With the Hogarth flask there is no such difficulty. The method of determination with the Hogarth flask is as follows:

A 10-gram portion of the 60-mesh coal or coke is weighed and is carefully introduced into the weighed flask with distilled water enough to fill the flask half full. The capacity of the Hogarth flasks as obtained on the market varies from 100 to 125 c. c. The flask is then placed on a small electric hot plate (fig. 11), in a 10-inch vacuum desiccator. The desiccator is evacuated by means of an aspirator or air pump. A current sufficient to keep the water boiling is passed through the hot plate. With an efficient vacuum pump all the air is

[a] Blair, A. A., The chemical analysis of iron, 7th ed., 1908, p. 278.

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expelled in 30 minutes. The flask is then removed from the desiccator, filled to the tubulure with recently boiled and cooled distilled water, and the stopper inserted. It is advisable to apply a thin film of vaseline to the stopper to prevent leakage.

After the flask has been cooled to about 25° C. in a water thermostat, distilled water that has been cooled in the same thermostat is drawn through the tubulure until the water level is slightly above the mark on the capillary of the stopper. This may be done without removing the flask from the thermostat by inserting the end of the tubulure in a small beaker of water and applying a slight suction on the stopper. The flask should remain in the thermostat until the temperature of contents is exactly 25° C. The water level is adjusted to the mark on the capillary by touching a piece of filter paper to the end of the tubulure or by drawing in a little water. The flask is then removed from the thermostat, wiped dry, and weighed. The true specific gravity is calculated as in the preceding method.

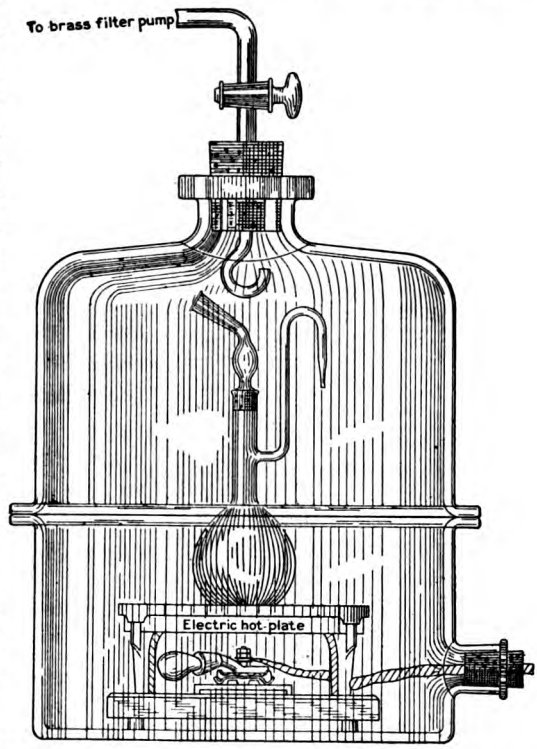

FIGURE 11.—Apparatus for determining true specific gravity.

The value for P is obtained by filling the flask with boiled water, cooling, and weighing, as described above.

By this method no difficulty is experienced in duplicating the figures for specific gravity to two decimal places.

DETERMINATION OF THE APPARENT SPECIFIC GRAVITY.

The apparatus used for determination of the apparent specific gravity consists of a galvanized-iron cylinder (fig. 12), which is filled with water to the water line, as indicated in the figure. In the cylinder is immersed a hydrometer made of brass. On the top of the hydrometer are two pans. The upper one is used for weights and the lower for the sample. Below the air buoy is a brass cage perforated with many holes to allow the air to escape when the instru-

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ment is immersed. The cage carries the sample when it is weighed under water.

The method of determining the apparent specific gravity is as follows: Brass weights are placed on the upper pan until the hydrometer sinks to a mark on the stem between the copper pan and the buoy. The total weight required is recorded. The weights are removed, and about 500 grams of the sample in lump form (about 1½ to 2 inch cubes) is placed in the copper dish. Brass weights are then added until the hydrometer sinks to the mark on the stem. The difference in the weights used gives the weight of the sample in air. The sample is then carefully transferred to the brass cage below the buoy. The weights on the upper pan are now adjusted until the instrument again sinks to the mark on the stem. The weight required to sink the hydrometer to the mark with no sample on the upper pan nor in the brass cage minus the weight required to sink it to the mark with the sample immersed in the cage equals the weight of the coke in water. Then,

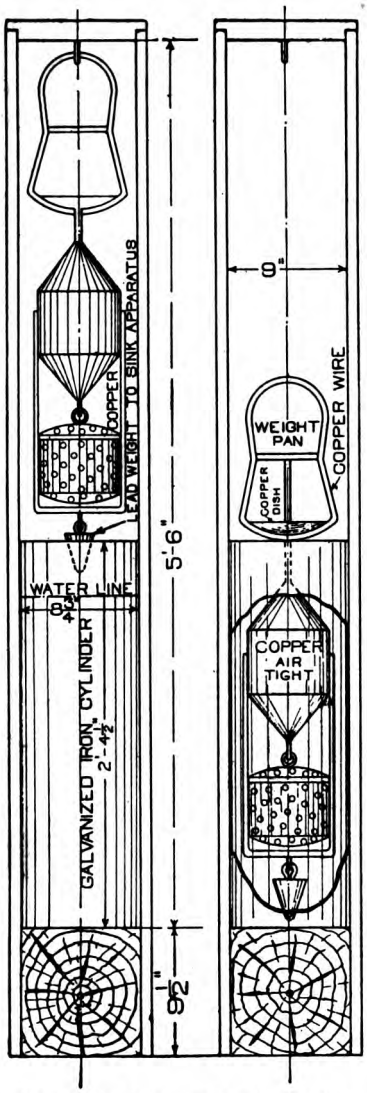

FIGURE 12.—Apparatus for determining apparent specific gravity.

If the weight of the sample in air $=x$
and the weight of the sample in water $=y$,
the apparent specific gravity $=\frac{x}{x-y}$

And

$100 \times \frac{\text{apparent specific gravity}}{\text{true specific gravity}} = \text{percentage}$ by volume of coke substance.

Also,

100 − percentage by volume of coke substance = percentage by volume of cell space.

In making apparent specific gravity determinations of coke the sample should preferably be in lumps of nearly the same size and shape. When the sample is immersed, the hydrometer should be moved rapidly up and down in the water a number of times in order

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to remove air bubbles. Since coke samples are porous, they take up water rapidly and should not be allowed to remain in contact with water more than five minutes during a determination. By observing the above-mentioned precautions satisfactory results can be obtained. All samples should be thoroughly dried before specific gravity determinations are made.

PUBLICATIONS ON FUEL TECHNOLOGY.

The following publications may be obtained without cost by applying to the Director, Bureau of Mines, Washington, D. C.:

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls.

BULLETIN 5. Washing and coking tests of coal at Denver, Colo., by A. W. Belden, G. R. Delamater, J. W. Groves, and K. M. Way. 1910. 62 pp.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker. 1911. 77 pp., 4 pls.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 51 pp., 1 pl.

BULLETIN 8. The flow of heat through furnace walls, by W. T. Ray and Henry Kreisinger. 1911. 32 pp.

BULLETIN 9. Recent development of the producer-gas power plant in the United States, by R. H. Fernald. 82 pp., 2 pls. Reprint of United States Geological Survey Bulletin 416.

BULLETIN 11. The purchase of coal by the Government under specifications, by George S. Pope. 80 pp. Reprint of United States Geological Survey Bulletin 428.

BULLETIN 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp.

BULLETIN 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls.

BULLETIN 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908–9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls.

BULLETIN 16. The uses and value of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl.

BULLETIN 19. Physical and chemical properties of the petroleums of the San Joaquin Valley, Cal., by I. C. Allen and W. A. Jacobs; with a chapter on analyses of natural gas from the southern California oil fields, by G. A. Burrell. 1911. 60 pp.

BULLETIN 21. The significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 62 pp. Reprint of United States Geological Survey Bulletin 367.

BULLETIN 24. Binders for coal briquets, by J. E. Mills. 56 pp. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 45 pp., 3 pls. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 28. Experimental work conducted in the laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 49 pp. Reprint of United States Geological Survey Bulletin 323.

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BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

BULLETIN 30. Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907–8, by C. L. Wright. 41 pp., 9 pls. Reprint of United States Geological Survey Bulletin 385.

BULLETIN 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp. Reprint of United States Geological Survey Bulletin 393.

BULLETIN 32. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

BULLETIN 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 49 pp. Reprint of United States Geological Survey Bulletin 403.

BULLETIN 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 32 pp. Reprint of United States Geological Survey Bulletin 412.

BULLETIN 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 28 pp. Reprint of United States Geological Survey Bulletin 402.

BULLETIN 37. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests and some foreign specifications for briquetted fuel, by W. F. M. Goss. 57 pp., 4 pls. Reprint of United States Geological Survey Bulletin 363.

BULLETIN 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion engines, by R. M. Strong and Lauson Stone. 1912. 243 pp., 3 pls.

BULLETIN 49. City smoke ordinances and smoke abatement, by S. B. Flagg. 1912. 55 pp.

BULLETIN 54. Foundry-cupola gases and temperatures, by A. W. Belden. 1913. 29 pp., 3 pls.

BULLETIN 55. The commercial trend of the producer-gas power plant in the United States, by R. H. Fernald. 1913. 93 pp., 1 pl.

BULLETIN 63. Sampling coal deliveries, and types of Government specifications for the purchase of coal, by G. S. Pope. 1913. 68 pp., 4 pls.

TECHNICAL PAPER 1. The sampling of coal in the mine, by J. A. Holmes. 1911. 18 pp.

TECHNICAL PAPER 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp.

TECHNICAL PAPER 3. Specifications for the purchase of fuel oil by the Government, with directions for sampling oil and natural gas, by I. C. Allen. 1911. 13 pp.

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